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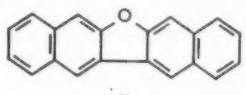
165. *The Synthesis of Dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan.*

By J. N. Chatterjea, R. F. Curtis, and S. P. Dhoubhadel.

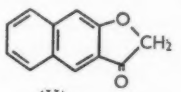
Dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan (I) has been synthesised unambiguously and compared with a sample prepared during attempts to obtain 2,3-6,7-dibenzodiphenylene. The furan (I) is also shown to be a by-product of the aerial oxidation of 2-naphthol in the presence of calcium ions.

The isolation of a by-product assumed to be dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan (I) in the preparation of 2,3-6,7-dibenzodiphenylene was described by Curtis and Viswanath.[1] The furan (I) has now been synthesised from 5,6-benzocoumaran-3-one (II) by the general procedure developed by Chatterjea [2] for β-brazans.

5,6-Benzocoumaran-3-one (II) [3] on treatment with nitrous acid in acetic acid gave 2-hydroxyimino-5,6-benzocoumaran-3-one; this was hydrolysed to 3-hydroxy-2-naphthylglyoxylic acid which was then cyclised with acetic anhydride (cf. Chatterjea [4]) to 5,6-benzocoumaran-2,3-dione (III). Condensation of the dione with phenacyl bromide in methanolic sodium methoxide produced methyl 2-benzoyl-5,6-benzocoumarone-3-carboxylate (IV). The acid (V) was converted into the acid chloride which was cyclised to dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan-1,4-dione (VI). Reduction with hydriodic acid gave the furan (I).



(I)



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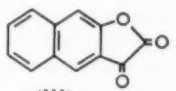
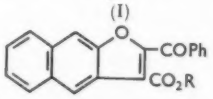
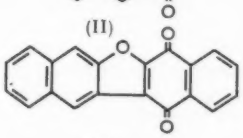


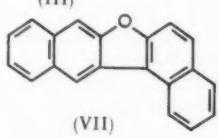
(III)



(IV) R = Me
(V) R = H



(VI)



(VII)

When this sample was compared with that originally prepared by Curtis and Viswanath [1] there were obvious differences, whereas the 2,4,7-trinitrofluorenone complexes prepared from the two samples were identical. Examination of the mass spectrum of the furan (I) prepared by the present method showed a highest significant molecular ion of mass number 268, corresponding to the molecular ion of $C_{20}H_{12}O$.- Significant breakdown ions occurred at masses 239 (probably parent minus CHO) and 237 (probably parent minus CH_3O) together with small, doubly charged ions corresponding to the same masses and an isotope peak at mass 269. These results are consistent with a strong ring structure such as the furan (I).

Mass spectra of the original sample obtained at 15 and 20 ev confirmed the presence of parent molecular ions of masses 252, 268, and 284. The molecular ion at 252 is 2,3:6,7-dibenzodiphenylene [1] inseparable by crystallisation and that at 268 is the furan (I). The molecular ion at mass number 284, $C_{20}H_{12}O_2$, gives only one significant breakdown ion of mass number 256 (probably due to loss of CO). This suggests by analogy with the furan (I) a strong ring structure, but it has not yet been possible to isolate this compound. The aerial oxidation of 2-naphthol at 340° in the presence of calcium ions leads to the dinaphthofuran (VII) as the major product.[5-8] A minor product is a compound, $C_{20}H_{12}O$, m. p. 300°,

[1] Curtis and Viswanath, *J.*, 1959, 1670, 3650.
[2] Chatterjea, *J. Indian. Chem. Soc.*, 1954, **31**, 101.
[3] Haberland and Kleinert, *Ber.*, 1938, **71**, 470.
[4] Chatterjea, *J. Indian. Chem. Soc.*, 1954, **31**, 194.
[5] Niederhausen, *Ber.*, 1882, **15**, 1123.
[6] Clemo and Spence, *J.*, 1928, 2811.
[7] Clemo, Cockburn, and Spence, *J.*, 1931, 1265.
[8] Buu-Hoï, *J.*, 1952, 489.

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which was investigated by Niederhausen[5] and Clemo.[6,7] Direct comparison with the dinaphthofuran (I) shows that these compounds are identical. The by-product is produced by oxidative coupling into the 3- rather than the 1-position of the second 2-naphthol molecule.

Revised spectral data are presented for the furan (I).

Experimental

5,6-Benzocoumaran-3-one (II).—This ketone was prepared by the acid-catalysed decomposition of 2-diazoacetyl-3-methoxynaphthalene.[3] The oxime, prepared in pyridine, crystallised from ethanol as plates, m. p. 212—214° (decomp.) with previous darkening (Found: N, 7·1. $C_{13}H_9O_2N$ requires N, 7·0%).

5,6-Benzocoumaran-2,3-dione (III).—The ketone (II) (6·5 g.) was treated at room temperature in acetic acid (100 c.c.) with sodium nitrite (12 g.) in small quantities during 4 hr. The mixture was diluted with water (100 c.c.) and the solid collected after 8 hr. *2-Hydroxyimino-5,6-benzocoumaran-3-one* (6·2 g.) crystallised from acetic acid as golden-yellow plates, m. p. 240° (decomp.) (Found: N, 6·5. $C_{13}H_7O_3N$ requires N, 6·6%).

The finely powdered oxime (6 g.) was triturated with concentrated hydrochloric acid (50 c.c.), the mixture filtered, and the solid dissolved in hot water (500 c.c.). The hot solution was filtered, concentrated, and then treated with concentrated hydrochloric acid (30 c.c.). 2-Hydroxy-3-naphthylglyoxylic acid was collected and boiled with acetic anhydride (15 c.c.) for a few minutes to give *5,6-benzocoumaran-2,3-dione* (III) (4·1 g.), orange red needles, m. p. 228° (from acetic acid) (Found: C, 72·9; H, 3·2. $C_{12}H_6O_3$ requires C, 72·7; H, 3·0%). With *o*-phenylenediamine in acetic acid, the *quinoxaline* derivative was obtained as golden-yellow needles, m. p. 330° (decomp.) (Found: C, 75·1; H, 4·4; N, 9·9. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2; N, 9·7%).

2-Benzoyl-5,6-benzocoumarone-3-carboxylic acid (V).—To a solution of the foregoing benzocoumarandione (3·5 g.) in methanolic sodium methoxide (0·45 g. of sodium in 30 c.c. of methanol), phenacyl bromide (3·5 g.) was added and the mixture was heated under reflux for 3 hr. On cooling, the solution deposited *methyl 2-benzoyl-5,6-benzocoumarone-3-carboxylate* (IV) (2·2 g.), prismatic needles, m. p. 118—119° (from methanol) (Found: C, 76·6; H, 4·4. $C_{21}H_{14}O_4$ requires C, 76·35; H, 4·3%). The corresponding *acid* crystallised from acetic acid as yellow prisms, m. p. 245° (Found: C, 75·8; H, 3·8. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%).

Dinaphtho(2,′3′-2,3)(2″,3″-4,5)furan-1′,4′-dione (VI).—A suspension of the preceding acid (1·2 g.) in benzene (10 c.c.) was heated with purified thionyl chloride (1·2 c.c.) for 20 min. After removal of benzene and thionyl chloride under reduced pressure, a solution of the acid chloride in carbon disulphide (40 c.c.) was cooled and treated with anhydrous aluminium chloride (4 g.). The mixture was kept for 6 hr. at room temperature, most of the solvent removed by decantation, and the aluminium complex decomposed with ice. The orange-red mass was collected, dried, and dissolved in benzene, and the solution chromatographed on alumina. The yellow band was eluted with benzene and concentrated, *dinaphtho(2′,3′-2,3)-(2″,3″-4,5)furan-1′,4′-dione* (VI) being obtained as an orange-red mass (0·2 g.) which was purified by sublimation in a vacuum. The pure quinone was formed as fine orange-red needles, m. p. 298—299° (Found: C, 80·2; H, 3·6. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). Reductive acetylation gave *1′,4′-diacetoxydinaphtho(2′,3′-2,3)(2″,3″-4,5)furan*, needles, m. p. 272° (from acetic acid) (Found: C, 74·6; H, 4·0. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%).

Dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan (I).—The quinone (0·05 g.) was boiled with freshly distilled hydriodic acid (15 c.c.) for 96 hr. The solid obtained on dilution was washed with hot sodium hydroxide solution, dried, and chromatographed in benzene on alumina. *Dinaphtho-(2′,3′-2,3)(2″,3″-4,5)furan* (I) crystallised from benzene as plates (0·025 g.), m. p. 308—310° (corr.); subliming at the m. p.) (Found: C, 89·6; H, 4·6; Mass number, 268. $C_{20}H_{12}O$ requires C, 89·5; H, 4·5%; *M*, 268).

The melting point of a mixture with a sample, m. p. 266°, prepared by Curtis and Viswanath[1] was m. p. 280—285°. A mass spectrum of the sample, m. p. 266°, showed mass number 268 together with compounds of mass number 252 and 284.

The furan shows in ethanol, $\lambda_{max.}$ (log ε) at 218 (4·41), 246 (4·67, shoulder), 254 (5·09), 272 (4·76), 279 (4·69), 290 (4·32), 300 (4·02), 318 (4·38), 335 (4·78), 359 (3·69), 379 (3·63) mμ; in

potassium bromide at 6·14(w), 6·67(w), 6·87(w), 7·45(w), 8·28(w), 8·66(w), 8·87(m), 10·52(m), 11·46(v.s.), 13·32(m), 13·50(v.s.) μ.

The 2,4,7-trinitrofluorenone complex crystallised from benzene in brownish red needles, m. p. 244—246° undepressed on admixture with the specimen obtained by Curtis and Viswanath.[1] Decomposition of the latter complex by sublimation (high vacuum at 160°) gave pure dinaphthofuran (I) the infrared spectrum of which was identical with a sample prepared by the synthetic method now described.

Dinaphtho(2′,3′-2,3)(2″,3″-4,5)*furan* (I) *from 2-Naphthol.*—2-Naphthol (100 g.) and calcium oxide (1 g.) were heated at 270° increasing to 320° during 8 hr. as described by Clemo *et al.*[6,7] The product was cooled and poured into excess of 20% sodium hydroxide, the mixture filtered, and the solid acidified and steam-distilled. The solid residue was collected and dried (29·5 g.), and from the alkaline filtrate 2-naphthol (60·5 g.) was recovered.

The crude product (1 g.) in benzene was passed through alumina (under ultraviolet illumination). The early fractions gave dinaphtho(2′,3′-2,3)(1″,2″-4,5)furan (VII) (460 mg.), pale yellow plates, m. p. 157° (from benzene) (Clemo and Spence [6] give m. p. 157°). Later fractions gave the furan (I), (31 mg.) as thin almost colourless plates (from benzene), m. p. (corr.) 310°; mixed m. p. with the synthetic specimen showed no depression and the infrared curves were identical.

Semimicroanalyses were by Mr. H. Mukherjee. Infrared spectra were determined by Mr. D. Jones, Swansea. Mass spectra were kindly determined by Imperial Chemical Industries Limited, Dyestuffs Division. One of us (S. P. D.) thanks the authorities of the Colombo Plan for a research scholarship.

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[*Received, May 5th,* 1960.]

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166. *The Methylation of 5α-Cholest-6-en-3-one: Further Examples of the Boat Conformation of Ring-A in the Steroids.*

By F. SONDHEIMER, Y. KLIBANSKY, Y. M. Y. HADDAD, G. H. R. SUMMERS, and W. KLYNE.

Methylation of 5α-cholest-6-en-3-one gives 2,2-dimethyl-5α-cholest-6-en-3-one, 2β-methyl-5α-cholest-6-en-3-one, and 2α-methyl-5α-cholest-6-en-3-one. Chemical evidence and optical rotatory dispersions indicate that in the first two products ring A is in a boat conformation.

THE discovery of 4-monomethyl sterols in natural plant [1] and animal [2,3] sources aroused interest, first, as to their significance in the biogenetic conversions of terpenes into sterols [4] and, secondly, as to their chemical synthesis from cholesterol. It has been shown that 5α-cholest-7-en-3-one with methyl iodide and potassium t-butoxide yields 4α-methyl-5α-cholest-7-en-3-one (lophenone),[2,5] rather than the 2α-methyl isomer which would have been expected by analogy with the methylation of 5α-cholestan-3-one under similar conditions.[6] This is undoubtedly a reflection of the fact the Δ^7-double bond causes the 3-keto-group to enolise towards $C_{(4)}$ rather than $C_{(2)}$, and it may be due to the extra strain in ring B caused by the olefinic linkage. It was of interest to study the methylation of

[1] Cox, King, and King, *Proc. Chem. Soc.*, 1957, 290; Djerassi, Krakower, Lemin, Liu, Mills, and Villotti, *J. Amer. Chem. Soc.*, 1958, **80**, 6284; Mazur, Weizmann, and Sondheimer, *Bull. Res. Council Israel*, 1958, **7**, *A*, 82; Amorós-Marin, Torres, and Asenjo, *J. Org. Chem.*, 1959, **24**, 411; Mazur, Weizmann, and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 6293.
[2] Wells and Neiderhiser, *J. Amer. Chem. Soc.*, 1957, **79**, 6569; *Arch. Biochem. Biophys.*, 1959, **81**, 300.
[3] Kandutsch and Russell, *J. Amer. Chem. Soc.*, 1959, **81**, 4114.
[4] Gautschi and Bloch, *J. Amer. Chem. Soc.*, 1957, **79**, 684.
[5] Mazur and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 6296.
[6] Mazur and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5220.

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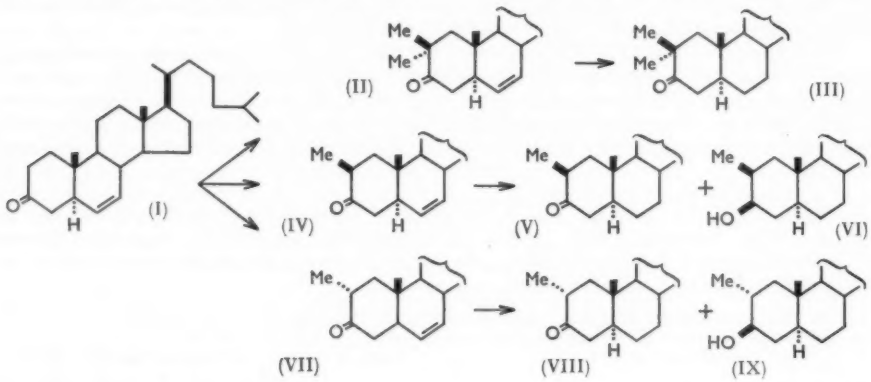
other cholestan-3-one derivatives unsaturated in ring B or C and in this paper we describe the results obtained with 5α-cholest-6-en-3-one (I) (independently by F. S. and Y. K. in Israel and by G. H. R. S. and Y. M. Y. H. at Swansea).

The ketone [7] (I) was obtained most conveniently by the oxidation of 5α-cholest-6-en-3β-ol [8] with chromium trioxide in pyridine.[9] Direct methylation of the ketone with methyl iodide and potassium t-butoxide in t-butyl alcohol under the conditions used previously [5] with the Δ^7-isomer, followed by chromatography, led to three new substances. The least polar was shown to be 2,2-dimethyl-5α-cholest-6-en-3-one (II), since hydrogenation in ethanol over palladium–charcoal yielded a compound with an infrared spectrum



($\lambda_{max.}$ 1703 cm.$^{-1}$ in CS_2) indicating it to be a dimethylated ketone; [6] this proved to be identical with 2,2-dimethyl-5α-cholestan-3-one [6,10] (III). A more polar substance proved to be 2β-methyl-5α-cholest-6-en-3-one (IV). Hydrogenation as before led to a monomethylated ketone ($\lambda_{max.}$ 1710 cm.$^{-1}$ in CS_2) which must be 2β-methyl-5α-cholestan-3-one (V) since its physical properties correspond to those of a known compound [6] and on acid treatment it was isomerised to 2α-methyl-5α-cholestan-3-one (VI), identical with an authentic sample [6,10] and also with the product of hydrogenation of the third ketone, 2α-methyl-5α-cholest-6-en-3-one (VII) isolated from the methylation.

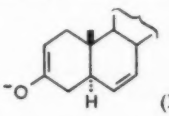
The catalytic hydrogenation of ketones (IV and VII) in acetic acid in the presence of palladium oxide also furnished respectively 2β- (VIII) and 2α-methyl-5α-cholestan-3β-ol (IX), their structures being confirmed by oxidation to their parent ketones (V and VI) by chromium trioxide in acetic acid. The 2β-methyl-5α-cholestan-3β-ol (VIII) was also obtained from 2β-methyl-5α-cholest-6-en-3-one by reduction with lithium aluminium hydride, followed by hydrogenation of the intermediate 2β-methyl-5α-cholest-6-en-3β-ol in ethanol in the presence of palladium–charcoal.

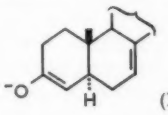
It had been expected that enolisation of the carbonyl group in ketone (I) would occur towards $C_{(2)}$, since the geometric relation between the double bonds in the resulting enol (X) is the same as in the above mentioned preferentially formed Δ^3-enol (XI) of 5α-cholest-7-en-3-one. The rate of condensation of ketone (I) with benzaldehyde,[11] which is much greater than that of the saturated 5α-cholestan-3-one, also indicates that the Δ^2-enol (X) is formed readily. The observed methylation of ketone (I) at position 2 is, therefore, in keeping with expectation.

On the other hand, the fact that one of the methylated products has the 2β-methyl

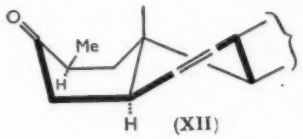
[7] Barton and Rosenfelder, *J.*, 1949, 2459.
[8] Wintersteiner and Moore, *J. Amer. Chem. Soc.*, 1950, **72**, 1923; James, Rees, and Shoppee, *J.*, 1955, 1370; Mazur, Nussim, and Sondheimer, *Proc. Chem. Soc.*, 1959, 314.
[9] Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.
[10] Mousseron, Winternitz, and de Paulet, *Compt. rend.*, 1957, **245**, 1859.
[11] Barton, McCapra, May, and Thudium, *J.*, 1960, 1297.

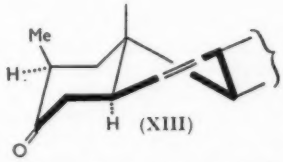
configuration was surprising. Although it has been shown that monomethylation of steroidal ketones may initially give the axial isomer,[12] the 2-methyl group in 2β-methyl-5α-cholest-6-en-3-one (IV) would be expected to epimerise under the strongly basic conditions if it were axially orientated since enolisation towards position 2 should occur


(X)


(XI)

fairly readily. Moreover, the ketone (IV) was unaffected on treatment with sulphuric acid in ethanol, conditions under which in the saturated series the axial 2β-methyl ketone (V) is readily epimerized to the equatorial 2α-isomer (VI).[6] Also 2α-methyl-5α-cholest-6-en-3-one (VII) was partially epimerised to ketone (IV) by this treatment. It, therefore, appears that the ketone (IV) possesses the stable configuration at position 2, *i.e.*, that the 2-methyl group is equatorial. It appears that this substance assumes a boat conformation in ring A (XII) rather than the usual chair conformation (XIII) and this is confirmed by the rotatory dispersion data discussed below.


(XII)


(XIII)

The rotatory dispersion curves of the saturated 3-oxo-5α-steroids with 2α- and 2β-methyl groups have been discussed by Djerassi *et al.*;[13] they show no abnormal features when considered in the light of the octant rule.[14]

The curve for the unsubstituted 5α-cholest-6-en-3-one shows an insignificant Cotton effect, superimposed on a strongly negative plain curve; this strong negative "background" has been found by Djerassi for the non-ketonic 5α-cholest-6-ene,[15] and also by us for 5α-cholest-6-en-3β-ol. The 2α-methyl-5α-cholest-6-en-3-one shows a rather similar curve; on the basis of the octant rule, it would be expected that the introduction of an equatorial methyl group would make a negligible change.

The 2β-methyl-5α-cholest-6-en-3-one, however, shows an unexpected *negative* Cotton effect (amplitude,[16] $10a^{-2} = -41$).

The octant rule would predict a more positive Cotton effect curve for a compound (XIII) than for the ketone (I). The negative curve seems compatible only with a boat (or modified boat) conformation of ring A (XII).

Since the corresponding saturated 2β-methyl-3-ketone gives a normal positive Cotton effect, we suggest that the preference for a boat in compound (XII) is due to some subtle stability change due to the 6,7-double bond.

The 2,2-dimethyl-5α-cholest-6-en-3-one (II) gives a somewhat stronger negative curve than the 2β-methyl derivative; this is consistent with a boat conformation for (II) [as (XII) with an additional 2α-methyl group, which would here be axial and make a negative contribution to the Cotton effect]. 2α-Bromo-2β-methyl-5α-cholestan-3-one also gives a negative Cotton effect, consistent with a boat conformation of ring A.[17]

[12] Beton, Halsall, Jones, and Phillips, *J.*, 1957, 753.
[13] Djerassi, Halpern, Halpern, and Riniker, *J. Amer. Chem. Soc.*, 1958, **80**, 4001.
[14] Moffit, Woodward, Moscowitz, Djerassi, and Klyne, unpublished work; cf. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, Chapter 13; Klyne in "Advances in Organic Chemistry" (ed., Raphael), Interscience, New York, Vol. I, 1960.
[15] Djerassi, Closson, and Lippman, *J. Amer. Chem. Soc.*, 1956, **78**, 3163.
[16] For nomenclature see Djerassi and Klyne, *Proc. Chem. Soc.*, 1957, 55.
[17] Djerassi, Finch, and Mauli, *J. Amer. Chem. Soc.*, 1959, **81**, 4997.

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The indeterminate curves of the unsubstituted 6,7-unsaturated 3-ketone (and its 2α-methyl derivative) suggest that these compounds may have an intermediate conformation (possibly the skew type discussed by Dreiding [18]), or they might be the result of a conformational equilibrium between chair and boat forms.

Experimental

$[\alpha]_D$ are for $CHCl_3$ solutions. Chromatograms were carried out with Merck " acid-washed " alumina by F. S. and Y. K. and with Spence alumina type " H " by Y. M. Y. H. and G. H. R. S. Where duplication of experiments has occurred, those performed by F. S. and Y. K. are given in sections (*a*).

5α-Cholest-6-en-3β-ol.—The alcohol was prepared by the methods of Mazur, Nussim, and Sondheimer [8] and of Corey and Gregoriou.[19]

5α-Cholest-6-en-3-one.—A solution of 5α-cholest-6-en-3β-ol (4 g.) in dry pyridine (75 ml.) was added gradually to chromium trioxide (3·7 g.) in pyridine (75 ml.), and the mixture was left at room temperature for 18 hr. The product was isolated with ether and was chromatographed on aluminium oxide (150 g.). Elution with pentane–benzene (3 : 1) gave 5α-cholest-6-en-3-one (1·94 g.) which on crystallisation from methanol had m. p. 121—122°, $[\alpha]_D$ −75° (Found: C, 84·1; H, 11·5. Calc. for $C_{27}H_{44}O$: C, 84·3; H, 11·5%) (lit.,[7] m. p. 116—117°, $[\alpha]_D$ −76°, −80°). Starting material (1·08 g.) was recovered from later fractions eluted with benzene–ether (9 : 1).

Methylation of 5α-Cholest-6-en-3-one.—(*a*) A solution of potassium (76 mg.) in t-butyl alcohol (7 ml.) was added to a boiling solution of 5α-cholest-6-en-3-one (400 mg.) in benzene (8 ml.) under nitrogen. Methyl iodide (0·4 ml.) in benzene (2 ml.) was then added and boiling under reflux was continued for a further 20 min. The mixture was cooled and poured on ice, and the product obtained by isolation with ether was chromatographed on alumina (16 g.). Elution with pentane yielded *2,2-dimethyl-5α-cholest-6-en-3-one* (148 mg.), which on crystallisation from methanol gave needles, m. p. 113—114°, $[\alpha]_D$ −67° (Found: C, 84·6; H, 11·4. $C_{29}H_{48}O$ requires C, 84·4; H, 11·7%).

Further elution with pentane yielded *2β-methyl-5α-cholest-6-en-3-one* (45 mg.), which on crystallisation from methanol gave m. p. 108—110° (depressed on admixture with the 2,2-dimethyl compound), $[\alpha]_D$ −69° (Found: C, 84·1; H, 11·55. $C_{28}H_{46}O$ requires C, 84·35; H, 11·6%).

(*b*) A boiling solution of 5α-cholest-6-en-3-one (1·82 g.) in benzene (36·5 ml.) was treated successively with potassium t-butoxide [prepared from potassium (380 mg.) and t-butyl alcohol (31 ml.)] and methyl iodide (1·8 ml.) in benzene (9 ml.). After being refluxed for 20 min. the mixture was poured on ice, extracted with ether, and worked up in the usual way to give a brown oil which crystallised. The product was chromatographed on aluminium oxide (110 g.). Elution with pentane–benzene (19 : 1) (6 × 100 ml.) gave an oil (79 mg.) which was not investigated further. Elution with pentane–benzene (9 : 1) (10 × 100 ml.) gave a solid (937 mg.) which on crystallisation from acetone–methanol gave 2β-methyl-5α-cholest-6-en-3-one as rods, m. p. 106—108°, $[\alpha]_D$ −68°, −69°, 60° (*c* 1·1, 0·9, 1·0) (Found: C, 84·3; H, 11·8%). Further elution with pentane–benzene (9 : 1) (9 × 100 ml.) gave a solid (243 mg.) which on crystallisation from acetone–methanol gave *2α-methyl-5α-cholest-6-en-3-one* as needles, m. p. 94—96°, $[\alpha]_D$ −65° (*c* 0·9) (Found: C, 83·9; H, 11·8. $C_{28}H_{46}O$ requires C, 84·35; H, 11·6%). Elution with pentane–benzene (8 : 2) (4 × 100 ml.) gave a solid (112 mg.) which on crystallisation from acetone gave crystals, m. p. 90—108°. Finally pentane–benzene (8 : 2) (10 × 100 ml.) eluted unchanged 5α-cholest-6-en-3-one (205 mg.), m. p. 118—119°, $[\alpha]_D$ −77°.

2,2-Dimethyl-5α-cholestan-3-one.—2,2-Dimethyl-5α-cholest-6-en-3-one (25 mg.) in ethanol (10 ml.) was shaken in hydrogen at room temperature over 10% palladium–charcoal (25 mg.). After 5 min. uptake of gas had stopped. The catalyst was removed, the solvent evaporated, and the residue crystallised from methanol. The resulting 2,2-dimethyl-5α-cholestan-3-one, m. p. 98—100°, $[\alpha]_D$ +79°, was identified with an authentic sample,[6,10] m. p. 99—100°, $[\alpha]_D$ +77°, through infrared comparison and non-depression of the m. p. on admixture (the m. p. 111—113° previously given for this substance [6] was an error).

[18] Dreiding, *Bull. Soc. chim. France*, **1960**, in the press; cf. Reeves, *Adv. Carbohydr. Chem.*, 1958, **15**, 27; Hasebrook and Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 87; Howlett, *J.*, 1957, 4353.
[19] Corey and Gregoriou, *J. Amer. Chem. Soc.*, 1959, **81**, 3127.

2β-*Methyl-5α-cholestan-3-one.*—(*a*) The hydrogenation of 2β-methyl-5α-cholest-6-en-3-one (20 mg.) in ethanol over palladium–charcoal was carried out as above. Crystallisation of the product from methanol gave 2β-methyl-5α-cholestan-3-one, m. p. 99—101°, $[\alpha]_D$ +84° (lit.,[6] m. p. 96—97°, $[\alpha]_D$ +86°).*

(*b*) 2β-Methyl-5α-cholest-6-en-3-one (140 mg.) in glacial acetic acid (30 ml.) was hydrogenated at room temperature in the presence of palladium oxide (56 mg.). The oily product was chromatographed on aluminium oxide (8 g.). Elution with pentane–benzene (9 : 1) gave a solid (21 mg.) which on crystallisation from methanol gave 2β-methyl-5α-cholestan-3-one, m. p. 95—97°. Elution with ether (3 × 20 ml.) gave a solid (113 mg.) which on crystallisation from methanol gave 2β-*methyl-5α-cholestan*-3β-*ol* as needles, m. p. 142—145°, $[\alpha]_D$ +26° (*c* 0·9) (Found: C, 83·3; H, 12·65. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%).

The alcohol (43 mg.) was oxidised in acetic acid (4 ml.) with a 2% solution of chromium trioxide in acetic acid (1 ml.). The product, a solid, crystallised from acetone–methanol to give 2β-methyl-5α-cholestan-3-one, m. p. 102—103°, $[\alpha]_D$ +78°, +82° (*c* 1·0, 0·7).

2β-*Methyl-5α-cholest-6-en*-3β-*ol.*—2β-Methyl-5α-cholest-6-en-3-one (145 mg.) in ether (50 ml.) was refluxed for 2 hr. with lithium aluminium hydride (150 mg.). The oily product was chromatographed on aluminium oxide (10 g.). Elution with benzene–ether (9 : 1) (4 × 20 ml.) gave a solid (121 mg.) which on crystallisation from acetone gave 2β-*methyl-5α-cholest-6-en*-3β-*ol*, m. p. 142—146°, $[\alpha]_D$ −97°, −95° (*c* 0·7, 1·0) (Found: C, 83·6; H, 11·9. $C_{28}H_{48}O$ requires C, 83·9; H, 12·1%). Further elution with benzene–ether (9 : 1) (3 × 20 ml.) gave fractions (total 29 mg.) which melted in the range 118—134°.

2β-*Methyl-5α-cholestan*-3β-*ol.*—2β-Methyl-5α-cholest-6-en-3β-ol (40 mg.) in ethyl acetate (15 ml.) was hydrogenated in the presence of palladium–charcoal (40 mg., 5%). The solid product, on crystallisation from ethyl acetate–methanol, gave 2β-methyl-5α-cholestan-3β-ol, m. p. 145—147°, $[\alpha]_D$ +23° (*c* 0·7), identical (infrared spectrum, mixed m. p.) with the specimen obtained above.

2α-*Methyl-5α-cholestan-3-one.*—(*a*) 2β-Methyl-5α-cholestan-3-one (12 mg.) in ethanol (2 ml.) containing a drop of 20% sulphuric acid was boiled under reflux for 2 hr. Isolation with ether and crystallisation from ether–methanol furnished 2α-methyl-5α-cholestan-3-one, m. p. 116—118°, $[\alpha]_D$ +35°. The m. p. was undepressed on admixture with an authentic sample,[6] and the infrared spectra were identical.

(*b*) 2α-Methyl-5α-cholest-6-en-3-one (120 mg.) in glacial acetic acid (20 ml.) was hydrogenated in the presence of palladium oxide (50 mg.) at room temperature. The product was chromatographed on aluminium oxide (8 g.). Elution with pentane–benzene (8 : 2) (5 × 25 ml.) gave a solid (110 mg.) which on crystallisation from acetone–methanol gave 2α-methyl-5α-cholestan-3-one as prisms, m. p. 119—120°, $[\alpha]_D$ +36° (*c*, 1·0). Elution with ether gave a solid (10 mg.) which on crystallisation from acetone–methanol gave 2α-methyl-5α-cholestan-3β-ol, m. p. 136°, $[\alpha]_D$ +10° (*c* 1·0) (lit.,[6] m. p. 139—140°, $[\alpha]_D$ +8°).

Epimerisation of 2α-*Methyl-5α-cholest-6-en-3-one.*—2α-Methyl-5α-cholest-6-en-3-one (18 mg.) in ethanol (4·5 ml.) containing 20% sulphuric acid (0·1 ml.) was heated under reflux for 4 hr. The product, on crystallisation from acetone–methanol, had m. p. 90—106° and after recrystallisation, m. p. 92—107°, $[\alpha]_D$ −70° (*c*, 1·0). The infrared spectrum of the product indicated it was a mixture of 2α- and 2β-methyl-5α-cholest-6-en-3-one.

2β-Methyl-5α-cholest-6-en-3-one on treatment with sulphuric acid in ethanol under the same conditions was recovered completely unchanged.

Optical Rotatory Dispersion Data.—General experimental details for the rotatory dispersion were as described by Jones and Klyne.[20] All curves were measured for methanol solutions (*c* 0·01) at 18—20°. All values are as molecular rotations.

2α-Methyl-5α-cholestan-3-one. Peak +2620 (305 mμ), trough, −3040 (275). Amplitude $10^{-2}a$, +57 (lit.,[13] $10^{-2}a$, +62).

2β-Methyl-5α-cholestan-3-one. Peak, +4080 (310 mμ), trough, −3840 (270). Amplitude +79 (lit.,[13] +73).

5α-Cholest-6-en-3-one. (No marked peak and trough) −380 (500 mμ); −2040 (308), −1650 (300), −3760 (260).

* *Added, January* 1, 1960.—Dr. A. Nickon, Johns Hopkins University, Baltimore, has recently prepared a specimen of 2β-methyl-5α-cholestan-3-one, m. p. 98—99° $[\alpha]_D$ + 122°, undepressed on admixture with our sample. We are very grateful to Dr. A. Nickon for this unpublished information.

[20] Jones and Klyne, *J.*, 1960, 871.

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2α-Methyl-5α-cholest-6-en-3-one. (Resembles preceding compound) −410 (500 mμ), −1200 (328), −890 (320), −2840 (275).

2β-Methyl-5α-cholest-6-en-3-one. Trough, −2900 (312 mμ), peak, +1160 (275). Amplitude, −41.

2,2-Dimethyl-5α-cholest-6-en-3-one. Trough, 4430 (312 mμ), peak +970 (275). Amplitude −54.

5α-Cholest-6-en-3β-ol. Negative plain curve; −615 (500 mμ), −1580 (350), −2720 (300).

We gratefully acknowledge grants from the Department of Scientific and Industrial Research, U.S. Army Research and Development Group in Frankfurt-am-Main (W. K), Parke-Davis and Co. Ltd., Detroit (G. H. R. S.). We are also indebted to Professor D. H. R. Barton, F.R.S., for valuable discussions, to Dr. B. A. Hems, Glaxo Laboratories Ltd., Greenford, Middlesex, for a gift of 7-dehydrocholesterol, and to Miss Jane Jackson for the polarimetric measurements.

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167. *Ligand Field Strengths of the Halide, Methyl, Phenyl, and Hydride Anions.*

By J. Chatt and R. G. Hayter.

The visible and ultraviolet spectra of compounds of the formula *trans*-$[RuXY\{C_2H_4(PMe_2)_2\}_2]$ (X = Y = Cl, Br, I, or CN; X = H, Me, Ph, or *p*-tolyl, and Y = Cl) have been determined and interpreted to show that the ligand field strengths of hydrogen and the organic groups are large, but less than that of cyanide ion.

Much is known about the relative crystal field (or ligand field) splittings of the halide ions and ligands containing oxygen and nitrogen as ligand atoms,[1,2] but nothing about the splittings caused by methyl or aryl groups and hydrogen atom when they take the place of anions in transition-metal complexes.

This arises because very few transition-metal complexes containing these groups as anionic ligands are known and even fewer provide the required information. However, the recently discovered alkyl, aryl, and hydrido-complexes of ruthenium [3] furnish useful material and here we record and discuss the ultraviolet spectra (Figs. 1—3) of the compounds *trans*-$[RuXY\{C_2H_4(PMe_2)_2\}_2]$ (X = Y = Cl, Br, I, CN; X = H, Me, Ph or *p*-tolyl, and Y = Cl).

It will be seen that the spectra have a number of intense bands at <340 mμ and in the case of the dihalides a further weak band ($\varepsilon < 100$) was resolved from the main bands. In the methyl, aryl, and hydrogen complexes the weak band has undergone a hypsochromic shift so that in the methyl and aryl compounds it is partially obscured by the intense bands and in the hydride it is completely obscured. By Gaussian analysis of the spectra,[4] the weak band in the methyl complex has been found exactly, and that in the phenyl complex rather less accurately, owing to an intense overlapping band ($\varepsilon_{max.}$ 8000). These " weak " bands are more intense than usual for internal *d*–*d*-transitions, but this may be due to mixing of the energy levels with those corresponding to the neighbouring intense bands. In the hydrogen complex, it is only possible to place a lower limit of 27,500 cm.$^{-1}$ on the energy of the weak band. In the spectra of the dichloro- and dibromo-complexes, the weak band fits a single Gaussian curve.

[1] Jorgensen, Report on the 10th Solvay Conference in Chemistry, Brussels, 1956.
[2] Orgel, (*a*) *J. Chem. Phys.*, 1955, **23**, 1004; (*b*) *J.*, 1952, 4756.
[3] Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153, and unpublished work.
[4] Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

The intense bands may be due to charge transfer and for the present study only the weak singlet bands (see Table) are of interest.

Wavelength ($\lambda_{max.}$; mμ), *energy E* (cm.$^{-1}$), *and intensity* ($\varepsilon_{max.}$) *of the lowest-energy singlet transition in the complexes* trans-[MXY{$C_2H_4(PMe_2)_2$}$_2$] (M = Ru, Os).

Compound	$\lambda_{max.}$	*E*	ε	Solvent
For M = Ru:				
X = Y = Cl	407	24,600	—	n-Hexane
	411	24,300	56	Benzene
	417	24,000	56	Ethanol
X = Y = Br	435	23,000	64	Ethanol
X = Y = I	455	22,000	87	Ethanol
X = Me, Y = Cl	348 *	28,700	123·5	Ethanol
X = Ph, Y = Cl	<344 *†	>29,100	280	Benzene
X = *p*-tolyl, Y = Cl	<352 †‡	>28,400	280	Benzene
X = H, Y = Cl	<364 *†	>27,500	—	n-Hexane
For M = Os:				
X = Y = Cl	350	28,600	88	Ethanol

* Estimated from Gaussian analysis. † These analyses consisted of complex overlapping bands, so that the values, although safely upper limits, are not certain. ‡ Estimated by comparison with corresponding phenyl compound.

Interpretation.—The ruthenium(II) complexes under study are diamagnetic and isoelectronic in the valency shell with cobalt(III) complexes. Thus their spectra should have two weak bands ($^1\Gamma_4$ and $^1\Gamma_5$) due to the forbidden $t_{2g} \longrightarrow e_g$ transition if all the ligand atoms were identical. In fact, our complexes are of the type *trans*-[RuA_4B_2] and *trans*-[RuA_4BC], so that we may expect the lower energy band ($^1\Gamma_4$) to be split in two.[2b] The amount of splitting is determined by the differences in the sum of the crystal-field contributions along each axis.[5] For the dihalogen complexes, these differences are probably large and the completely resolved band (Fig. 1) will be the lower-energy component $^1\Gamma_{5t}$. If we assume that the partly obscured band in the spectrum of the dichloro- and dibromocomplexes is the higher-energy component $^1\Gamma_{2t}$, the splitting is 9000—10,000 cm.$^{-1}$ and, in any case, this represents a lower limit. This splitting is larger than is observed for related complexes, where the differences between the ligands are less marked, for example, *trans*-$[CoCl_2(NH_3)_4]^+$ (5100 cm.$^{-1}$) and *trans*-$[CoCl_2\ en_2]^+$ (6400 cm.$^{-1}$).[6]

The spectrum of the corresponding osmium complex, *trans*-[$OsCl_2${$C_2H_4(PMe_2)_2$}$_2$] (Fig. 3) was also examined. However, the separation between the weak and intense bands was too small to permit the determination of the relative ligand-field splittings of the hydride and organic anions. The singlet ⟶ triplet transition expected to accompany the $^1\Gamma_4$ singlet ⟶ singlet transition was, in general, not observed in the spectra of the ruthenium complexes. It was, however, visible in the spectrum of the osmium compound as a weak shoulder ($\varepsilon \sim 13$) on the low-energy side of the weak resolved band. This accords with the general observation that the triplet band is more intense in the complexes of the very heavy metals.

Discussion.—The very large hypsochromic shift (>4100 cm.$^{-1}$) of the low-energy band when chlorine is replaced by alkyl or aryl as ligand indicates the much greater ligand-field strengths of the organic groups than of chloride ion. Similarly, the replacement of chlorine by hydrogen caused a shift of at least 2900 cm.$^{-1}$, indicating that the latter also has a strong ligand field. A direct comparison between, say, methyl and cyanide ion is not possible owing to failure to prepare a *trans*-halide cyanide. However, a rough estimate of the minimum energy of the $^1\Gamma_{5t}$ transition in the (unknown) complex *trans*-[RuCl·CN{$C_2H_4(PMe_2)_2$}$_2$] can be made from the spectra of the corresponding dicyano- and dichloro-complexes, since ligand-field effects in mixed complexes can be averaged.[1] The weak band in *trans*-[$Ru(CN)_2${$C_2H_4(PMe_2)_2$}$_2$],H_2O probably does not occur at any energy lower than that corresponding to $\varepsilon = 50$ (34,400 cm.$^{-1}$) in its spectrum. This fixes

[5] Basolo, Ballhausen, and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 810, and references therein.
[6] Linhard and Weigel, *Z. anorg. Chem.*, 1952, **271**, 101.

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the minimum energy for the corresponding band in the chloride cyanide at $\frac{1}{2}(34{,}400 + 24{,}000) = 29{,}200$ cm.$^{-1}$, which is close to, but greater than, that of the lowest-energy band in the spectrum of the methyl complex (28,700 cm.$^{-1}$). It appears that the methyl group, although it has a large ligand field strength, is weaker than cyanide ion.

Now the position of a ligand in the spectrochemical series is determined [1] mainly by the ligand atom nearest to the metal, the ligand field strength increasing halogen < O < N < C. The current results indicate that alkyl and aryl groups as ligands may be grouped with cyanide, previously the only ligand with carbon as ligand atom to have been placed in the series. The higher ligand field strength of cyanide ion might be attributed

Ultraviolet and visible spectra.

FIG. 1. FIG. 2. FIG. 3.

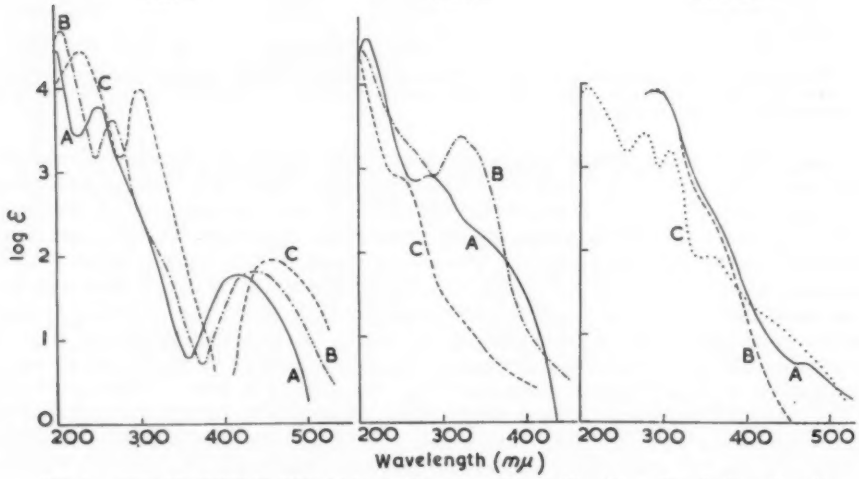

FIG. 1. *trans*-[RuXY{$C_2H_4(PMe_2)_2\}_2$]: A, X = Y = Cl; B, X = Y = Br; C, X = Y = I. (All in EtOH.)

FIG. 2. *trans*-[RuXY{$C_2H_4(PMe_2)_2\}_2$]: A, X = Me, Y = Cl (in EtOH); B, X = H, Y = Cl (in n-hexane); C, X = Y = CN (in EtOH).

FIG. 3. *trans*-[MXY{$C_2H_4(PMe_2)_2\}_2$]: A, M = Ru, X = Cl, Y = *p*-tolyl (in C_6H_6); B, M = Ru, X = Cl, Y = Ph (in C_6H_6); C, M = Os, X = Y = Cl (in EtOH).

to its capacity to form double bonds with metals such as ruthenium(II). Nevertheless the identity of the ligand atom itself, as required by the older electrostatic concept of crystal field theory, must be a major factor, since methyl, which could not form strong double bonds, has a high strength. This suggests that all ligands with carbon as ligand atoms may have high ligand field strengths.

Experimental.—Preparation of the compounds studied in this paper will be detailed later.[3] The spectra were measured on a Unicam S.P. 500 spectrophotometer with n-hexane (" Special for Spectroscopy "), absolute ethanol (Burrough's), and benzene (dried with calcium chloride and by distillation from phosphorus pentoxide) as solvents. The solutions were accurately prepared to be about 10^{-3}M and the spectra measured at 21° ± 1°.

The authors thank Dr. L. E. Orgel for valuable discussion and Messrs. M. Parry, D. H. Goschenhofer, and M. L. Searle for experimental assistance.

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[*Received, August 18th,* 1960.]

168. *Studies on Transition-metal–Nitric Oxide Complexes. Part VI.* Platinum, Palladium, and Nickel Complexes.*

By W. P. Griffith, J. Lewis, and G. Wilkinson.

Several new six-co-ordinate nitric oxide complexes of platinum(II) and palladium(II) and four- and six-co-ordinate nickel(II) complexes are reported.

The infrared criterion for co-ordination of nitric oxide to a transition metal as an NO^- group, a band at *ca.* 1100 cm.$^{-1}$, has been confirmed by isotopic substitution.

This paper is concerned with nitric oxide complexes of platinum(II), palladium(II), and nickel(II). The new compounds together with their infrared spectra are listed in Table 1.

Since several of the complexes could have been formulated with NO^- rather than NO^+ co-ordination, we have also attempted by use of ^{15}N as tracer to confirm that such NO^- complexes show a weak to moderately strong peak in the region of 1100 cm.$^{-1}$.

Table 1. *Infrared spectra (cm.$^{-1}$) of* Pt–, Pd–, *and* Ni–*nitric oxide complexes.*

Complex	NO stretch	Other strong bands
$K_2[Pt(NO)Cl_5]$ *	1711	—
$Na_2[Pt(NO)Cl_5]$ †	1765	—
$K_2[Pt(NO)(CN)_5]$ †	1720	2110 (CN)
$K_2[Pt(NO)(NO_3)_4Cl]$ *	1720	1320 and 835 (NO_3)
$K_2[Pt(NO)(NO_3)_4(NO_3)]$ *	1775	1350 and 840 (NO_3); 1500, 1260, 970, 940 and 815 (NO_3)
$Cs_2[Pt(NO)(NO_3)_4(NO_3)]$ *	1720	
$[Pt(NO)(en)_2Cl]Cl_2$ †	1750	1645, 1590 and 1300 (en)
$[Pt(NO)(NH_3)_4Cl]Cl_2$	1670	1620, 1530, 1330, and 910 (NH_3)
$[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$ *	1725	1615, 1560 (NH_3); 1040, 940, 825 (NO_3)
$[Pt(NO)(NH_3)_4(OAc)]Cl_2$ *	1690	1560, 1500, 900, 820 (NH_3 and OAc^-)
$[Pt(py)_2(NO_2)Cl]$	—	1300, 830, and 825 (NO_2); 1620, 1210, 1150, 1065, and 760 (py)
$(pyH)_2[PtCl_4]$	—	1610, 1210, 1060, and 760 (py)
$[Pt(NH_3)_2Cl_2]$	—	1620, 1590, 1240, 900 (NH_3)
$[Pt(NH_3)_4(SO_4)]Cl_2$ *	—	1620, 1590, 1240 (NH_3); 1080 (SO_4)
$K_2[Pd(NO)(NO_3)_4(NO_3)]$ *	1720	1300 and 800 (NO_3); 1500, 1280, 1010, 995, and 790 (NO_3)
$[Pd(NO)_2(NO_3)_2]$ †	1810, 1780	1500, 1300, 990, 820 (NO_3)
$[Ni(NO)(NH_3)_3(OH)](OH)_2$ *	1780	3500 (OH); 1615 (NH_3)
$[Ni(NO)(NH_3)(OCH_3)(OH)](OH)$ *	1785	3500 (OH); 1615 (NH_3)
$[Ni(NO_3)(OH)(MeOH)]_2,2H_2O$ *	—	3500 (OH); 1630, 1030, 790 (MeOH); 1410, 1250, 830 (NO_3)

All spectra taken in Nujol mulls.
* New compounds prepared in this work. † Not pure.
en = ethylenediamine; OAc = acetate; py = pyridine.

(A) *Platinum Complexes.*—The only nitric oxide complexes of platinum studied previously are

$K[Pt(NO)Cl_3]$,[1] $[Pt(NO)pyCl_2]$,[1] $[Pt(NH_3)_4][Pt(NO)Cl_3]_2$,[1] $[Pt(NO)(NH_3)_4Cl]Cl_2$,[2-4]

and an ill-defined series of products such as $[Pt(NO)(NH_3)_3(HSO_4)_{1\cdot5}(SO_4)_{0\cdot5}Cl_{0\cdot5}]$.[4]

(a) *The action of nitric oxide on aqueous solutions of potassium chloroplatinate*(II). It was reported by Gelman and Maximova [1] that nitric oxide, when shaken with a neutral solution of potassium chloroplatinate(II), gave a green complex (not isolated) which they formulated as $K[Pt(NO)Cl_3]$. It was claimed that this could be precipitated, by addition of

* Part V, *J.*, 1959, 1775.

[1] Gelman and Maximova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 748.
[2] Hadow, *J.*, 1866, **19**, 345.
[3] Jensen, 5th Nord. Kemikermøde Forh., 1939, 200.
[4] Koefoed, "Om nogle Nitroso Platinammoniakforbindelser," Akad. Afh. Kopenhagen, 1894, pp. 32, 500.

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tetrammineplatinum(II) chloride, as $[Pt(NH_3)_4][Pt(NO)Cl_3]_2$, or by addition of pyridine to give $[Pt(NO)pyCl_2]$.

These experiments have been repeated. Neutral or acidic aqueous solutions of potassium chloroplatinate(II) slowly absorbed nitric oxide over a period of 24 hours, to give deep-green solutions. Alkaline solutions (pH >9) did not absorb the gas.

Addition of pyridine to the green solution gave yellow dipyridinenitrochloroplatinum(II), $[Ptpy_2(NO_2)Cl]$. This substance was diamagnetic, and its infrared spectrum has strong peaks in the nitro-region (825 and 1300 cm.$^{-1}$),[5] but no nitrosyl absorption bands. It therefore seemed likely that the equilibration, $NO^+ + OH^- \rightleftharpoons NO_2^- + H^+$, observed in nitroprussides [6] and in nickelnitrosyl alcoholate complexes [7] had occurred, the equilibrium having been shifted to the right by the strongly basic pyridine. An attempt to reverse the equilibrium by the addition of hydrochloric acid gave the complex $(pyH)_2[PtCl_4]$.

Addition of tetrammineplatinum(II) chloride to the green solution gave a purple, diamagnetic complex for which consistent analyses could not be obtained. The infrared spectrum of this product showed peaks at 825 and 1300 cm.$^{-1}$ and at 1750 cm.$^{-1}$; similar results were obtained with other precipitants such as cæsium chloride and tetraphenylarsonium chloride. It seems likely that the green solution which results from the reaction of nitric oxide with chloroplatinate(II) ion contains a mixture of a nitro- and a nitrosyl complex. However, the presence of a simple salt $K[Pt(NO)Cl_3]$ seems unlikely in view of the diamagnetism of the solution and the precipitated solid, and if this stoicheiometry is correct it would appear more likely that a polymeric species has been obtained.

(b) *The reaction of nitrosyl chloride with platinum*(II) *complexes.* It was found that a solution of nitrosyl chloride in chloroform reacted with a number of four-co-ordinated platinum(II) complexes to give compounds of the general type $[Pt^{II}(NO)X_5]$. The following new complexes were prepared by this method: $K_2[Pt(NO)Cl_5]$, $K_2[Pt(NO)(NO_2)_4Cl]$, and $[Pt(NO)en_2Cl]Cl_2$. Spectral evidence was obtained for the existence of $Na_2[Pt(NO)Cl_5]$ and $Na_2[Pt(NO)(CN)_5]$. There was no reaction, or decomposition followed, when nitrosyl chloride in chloroform was shaken with the following complexes: $K_2[Pt(CNS)_4]$, $[(C_2H_4)PtCl_2]_2$, and R_2PtCl_2, where R = Ph_3P, $Pr^n{}_3P$, $Bu^n{}_3P$, or Ph_3As.

These new compounds were made by shaking a suspension of the platinum(II) complexes for 24 hours with nitrosyl chloride in chloroform. The green products decomposed slowly in water to give platinum(IV) complexes. They were diamagnetic, and all showed strong infrared bands near 1700 cm.$^{-1}$, suggesting that the nitric oxide is found as a co-ordinated nitrosonium ion.[8]

These complexes may contain either five- or six-co-ordinated platinum(II), *e.g.*, $K_2[Pt(NO)Cl_5]$ or $K[Pt(NO)Cl_4]$,KCl, $[Pt(NO)en_2Cl]Cl_2$ or $[Pt(NO)en_2]Cl_3$. It was impossible, owing to the insolubility of some of the products, to carry out molecular-weight or conductivity determinations. Very few six-co-ordinate platinum(II) complexes have been reported;[9-11] such a structure is favoured, however, for the following reasons: (i) polarographic and conductimetric measurements on the complex $[Pt(NO)(NH_3)_4Cl]Cl_2$, prepared by the action of nitrosyl chloride in chloroform on $[Pt(NH_3)_4]Cl_2$, confirm that this compound contains six-co-ordinated platinum(II) (see below); (ii) an *X*-ray powder photograph of $K_2[Pt(NO)Cl_5]$ showed no lines which could be attributed to KCl; (iii) the alternative formulation of these compounds as six-co-ordinate platinum(IV) complexes with the nitric oxide co-ordinated as NO^- is eliminated by the infrared spectra, the NO^- ligand absorbing near 1100 (see below and ref. 12) and NO^+ near 1800 cm.$^{-1}$.[8]

[5] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[6] Cambi and Szegö, *Atti R. Accad. Lincei*, 1927, **5**, 737.
[7] Griffith, Lewis, and Wilkinson, *J.*, 1959, 1775.
[8] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[9] Harris, Nyholm, and Stevenson, *Nature*, 1956, **177**, 1127.
[10] Harris, Livingstone, and Reece, *J.*, 1959, 1505.
[11] Brosset, *Arkiv Kemi, Min., Geol.*, 1948, **25**, No. 19.
[12] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

(c) *Nitrosyltetramminechloroplatinum*(II) *dichloride*, $[Pt(NO)(NH_3)_4Cl]Cl_2$. This complex has been prepared [2-4] by the action of nitric oxide on a solution of tetrammineplatinum(II) chloride in moderately strong hydrochloric acid. It may also be prepared, in a manner analogous to that used for the complexes discussed in the last section, by the action of a solution of nitrosyl chloride in chloroform on a suspension of $[Pt(NH_3)_4]Cl_2$. The complex is green and diamagnetic, and is moderately soluble without decomposition in water.

The infrared spectrum of the complex showed a strong peak at 1670 cm.$^{-1}$, attributed to a N–O stretch; no absorption was found near 1100 cm.$^{-1}$ which could be attributed to NO^- or hyponitro-groups. Conductivity measurements in water indicated that the complex was a 2 : 1 electrolyte.

Polarographic reduction of the complex in 0·1N-potassium chloride at the dropping-mercury electrode gave a single, well-defined irreversible cathodic wave ($E_{\frac{1}{2}} = -1{\cdot}05$ v *versus* S.C.E.). The concentration of the complex was proportional to the diffusion current (see Table 2) and, from a comparison of the diffusion current constant, I, with that found for other platinum(II) ammines [13] and also from the value of the half-wave potential, it is clear that the wave corresponds to a reduction of platinum(II) to platinum(0). Since the characteristic three-stepped reduction wave for the nitrosyl ligand, as found in polarography of the nitroprusside ion,[14,15] is not observed here, it seems likely that the reduced product is a platinum(0)–nitrosyl complex {possibly $[Pt(NO)(NH_3)_2Cl]$} rather than metallic platinum. A similar situation has been observed in polarographic reduction of $K_3[Cr(NO)(CN)_5]$.[16] It has been shown [13,17] that when platinum(II) ammines are reduced at the dropping electrode to platinum metal, no diffusion-current maximum is observed in most cases. The nitrosyl complex, when reduced polarographically in 0·1N-potassium hydroxide, gave no diffusion-current plateau but did give a decomposition voltage (E^*) at about −1·55 v (versus S.C.E.), as found for tetrammineplatinum(II) chloride.[13] It, therefore, seems likely that in basic solution, when the nitrosyl complex has changed into the nitro-form, polarographic reduction to platinum metal takes place.

TABLE 2. *Polarographic reduction of* $[Pt(NO)(NH_3)_4Cl]Cl_2$ *at* 22° C.

(a) *Reduction with* 0·1N-KCl *as base electrolyte.*

Conc. of complex (mmole/l.)	1·3	0·60	0·32	0·15
i_d (in μA.)	6·0	2·7	1·5	0·70
$i_d/cm^{\frac{1}{2}}t^{\frac{1}{6}}$	2·01	1·95	2·04	2·03
$E_{\frac{1}{2}}$ (*vs.* S.C.E.)	−1·06	−1·04	−1·04	−1·04

(b) *Reduction with* 0·1N-KOH *as base electrolyte.*

Conc. of complex (mmole/l.)	3·12	1·55	0·70	0·30	0·10
E^* (*vs.* S.C.E.)	−1·60	−1·58	−1·55	−1·50	−1·50

(d) *Potassium nitrosyltetranitronitratoplatinate*(II), $K_2[Pt(NO)(NO_2)_4(NO_3)]$. It has been reported [17] that potassium tetranitroplatinate(II) reacts with nitric acid to give $K_2[Pt(NO_2)_3(NO_3)_3]$, which is hydrolysed by water to $K_2[Pt(NO_2)_3(NO_3)_2(OH)]$.

It was found that potassium tetranitroplatinate(II) dissolved in concentrated nitric acid to give a deep blue solution from which no solid blue products could be isolated. The infrared spectrum of this solution showed a peak at 1750 cm.$^{-1}$. Evaporation of the blue solution on a steam-bath gave yellow crystals (which redissolved in water to give a yellow solution), $K_2[Pt(NO)(NO_2)_4NO_3)],2H_2O$. The complex was diamagnetic, and its infrared spectrum showed peaks typical of co-ordinated nitrato- and nitro-groups (see Table 3 and

[13] Hall and Plowman, *Austral. J. Chem.*, 1956, **9**, 14.
[14] Zuman and Kabat, *Coll. Czech. Chem. Comm.*, 1954, **19**, 873.
[15] Lanza and Corbellini, *Contr. Tecr. e Sper. di Polarographia, Padova*, 1951, 133.
[16] Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.
[17] Tscherjajev and Hening, *Izvest. Inst. Isuceniju Platiny*, 1933, **11**, 46.

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ref. 18) together with a peak at 1675 cm.$^{-1}$ attributed to a nitrosyl group. Conductivity measurements in water showed it to be a 2 : 1 electrolyte.

(e) *Miscellaneous platinum complexes.* Reactions of tetrammineplatinum(II) chloride in moderately concentrated nitric or acetic acids with nitric oxide gave the complexes $[Pt(NO)(NH_3)_4(OAc)]Cl_2$ and $[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$. The infrared spectrum of the latter complex contains bands [18] typical of a co-ordinated nitrate group, and the given formulation is therefore preferred, although the formulation $[Pt(NO)(NH_3)_4Cl](NO_3)_2$ seems a possibility. It is difficult to be certain whether the acetate group is bound as a co-ordinated group.

According to Koefoed,[4] the complex $[Pt(NH_3)_2(NO_2)_2]$ reacts with hydrochloric acid to give $[Pt(NO)(NH_3)_2Cl]_{0\cdot75},H_2O$; and also $[Pt(NO)(NH_3)_4Cl]Cl_2$ reacts with sulphuric acid to give $[Pt(NO)(NH_3)_3(HSO_4)_{1\cdot5}(SO_4)_{0\cdot5}Cl_{0\cdot5}]$. Both these products were examined analytically and spectroscopically; neither gave nitro- or nitrosyl peaks in the infrared spectrum, and analyses showed the products to be respectively $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_4SO_4]Cl_2$. (The latter showed a peak at 1080 cm.$^{-1}$, attributed to an SO_4^{2-} group.)

(B) *Nitrosyl Complexes of Palladium.*—The only known palladium nitrosyl complexes are $[Pd(NO_2)Cl_2]$, $[Pd(NO)_2SO_4]$,[7,19] and $[Pd(NO)Cl]_n$.[20]

(a) *Potassium nitrosyltetranitronitratopalladate*(II), $K_2[Pd(NO)(NO_2)_4(NO_3)]$. This new compound was prepared in the same way as the analogous platinum complex by treating potassium tetranitropalladate(II) with nitric acid. The red crystalline product was diamagnetic and its infrared spectrum gave peaks in the co-ordinated nitro- and nitrato-regions, as well as a peak at 1720 cm.$^{-1}$. A comparison of the infrared spectra of known nitrosyl-nitro-nitrato-complexes shows several similarities (Table 3).

TABLE 3. *Infrared spectra of nitrosyl-nitro-nitrato-complexes.*

Complex	Frequencies (cm.$^{-1}$)							
$K_2[Pd(NO)(NO_2)_4(NO_3)]$	1720	1500	1300	1280	1010	995	800	790
$K_2[Pt(NO)(NO_2)_4(NO_3)]$	1675	1500	1350	1260	970	940	840	815
$[Ru(NO)(NO_2)_2(NO_3)(H_2O)_2]$ [21]	1931	1504	1300 [a]	1276	989	—	863, 833	786
Assignments made by Fletcher *et al.*[21]	NO	NO_3	—	NO_3	RuNO	—	NO_2	NO_3
Preferred assignments [b]	NO	NO_3	NO_2	NO_3	NO_3	NO_3	NO_2 or	NO_3

[a] Although Fletcher *et al.* list no peak at this frequency, the reproduction of the original spectrum in the paper clearly shows the presence of this band. [b] On the basis of the report by Gatehouse *et al.*[18] that co-ordinated nitrato-groups have bands near 1500, 1280, 1000, and 790 cm.$^{-1}$.

(b) *Other palladium nitrosyl complexes.* Although there was some evidence of a reaction between nitrosyl chloride in chloroform with $K_2[Pd(CN)_4]$ and $[Pd(NH_3)_4]Cl_2$, and of reaction between nitric oxide and a solution of tetramminepalladium(II) chloride in hydrochloric acid, no pure products could be isolated.

According to Manchot and Waldmüller,[19] nitric oxide and methanol vapour react with solid palladous nitrate to give palladous nitrite, $Pd(NO_2)_2$. This work was repeated by us. The black diamagnetic product gave two peaks in the infrared nitrosyl region (1810 and 1780 cm.$^{-1}$), together with peaks identical with those given by palladous nitrate. Analyses were variable, but the complex may be $[Pd^0(NO)_2(NO_3)_2]$, analogous to the dinitrosyl chloride and sulphate.[7,19]

(C) *Nitrosyl Complexes of Nickel.*—(a) *Nitrosyldi-amminehydroxynickel*(II) *hydroxide*, $[Ni(NO)(NH_3)_2OH](OH)_2$. It is reported [22] that a mixture of nitric oxide and ammonia gases reacts with nickel carbonyl in the presence of water to give the complex

[18] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[19] Manchot and Waldmüller, *Ber.*, 1926, **59**, 2363.
[20] Schmidt and Jira, *Chem. Ber.*, 1960, **93**, 162.
[21] Fletcher, *Ricerca sci.*, 1958, **28** (Suppl.), 1.
[22] Frazer and Trout, *J. Amer. Chem. Soc.*, 1936, **58**, 2203.

$[Ni(NO)(NH_3)_5](NO_2)_2$. The preparation was repeated and a blue, amorphous product was obtained. The complex was paramagnetic with a moment of 2·9 B.M. at room temperatures, and the infrared spectrum showed bands at 3500 cm.$^{-1}$ (OH stretch), 1620 cm.$^{-1}$ (NH_3), and at 1780 cm.$^{-1}$ (NO). The analyses correspond to the formulation $[Ni(NO)(NH_3)_2(OH)](OH)_2$ or $[Ni(NO)(NH_3)_2(OH)_3]$. The blue colour [23] favours the former structure, in which case the complex is a direct analogue of $[Ni(NO)(OH)_3]$.[7] Although it has been pointed out that colour is in itself not diagnostic of tetrahedral nickel(II),[23] the extinction coefficients for $[Ni(NO)(OMe)_2(OH)]$ (at 650 mμ) and $[Ni(NO)(NH_3)(OMe)(OH)](OH)$ (see below) (at 637 mμ) were 99·1 and 56·0, respectively. These high values for ε are reasonable for a tetrahedral structure, and also by analogy the related compounds have been considered as tetrahedral.

(b) *Nitrosylamminehydroxymethoxynickel*(II) *hydroxide*, $[Ni(NO)(NH_3)(OMe)(OH)](OH)$. This new compound was prepared by passing a mixture of dry ammonia and nitric oxide into a methanolic solution of nickel carbonyl. It was blue and slightly soluble in water—in which it quickly decomposes—and in methanol. It was paramagnetic (see Table 4)

TABLE 4. *Magnetic measurements on solid* $[Ni(NO)(NH_3)(OMe)(OH)(OH)]$.

Temp. (°K)	295·6	271·0	258·0	231·5	214·0	184·0	163·5	137·0	118·0	103·0
$10^3\chi_A$ (c.g.s.u.)	3·63	4·13	4·32	4·76	5·29	5·94	6·50	7·25	8·58	9·48
$10^{-3}\chi_A^{-1}$	2·75	2·42	2·31	2·10	1·89	1·68	1·54	1·38	1·17	1·05

Diamagnetic correction for metal atom and ligands: -40×10^{-6} c.g.s.u.

with a moment of 3·14 B.M. and a θ of +27°, indicating that the nickel atom has two unpaired electrons.

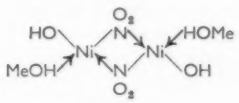
The infrared spectrum showed peaks in the OH stretching region (3500 cm.$^{-1}$), NH_3 region (1615 cm.$^{-1}$) and NO region (1785 cm.$^{-1}$) in addition to methanol peaks. The visible spectrum of a solution of the complex in methanol showed a peak at 637 mμ (ε 56). There was no evidence of isomerisation of the blue solid to a green nitro-compound as there was in the case of $[Ni(NO)(OH)(OMe)_2]$,[7] but a solution in methanol did isomerise to the green form (see below) when kept for longer than 24 hours. The ethanol and propanol complexes could not be obtained pure.

The structure which best accords with the spectral and magnetic data is

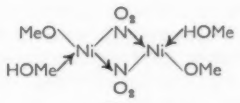
$$[Ni^{II}(NO)(NH_3)(OMe)(OH)](OH)$$

involving tetrahedral nickel.

(c) *Dimethanolate* μμ′*-dinitro-nickel*(II) *dihydroxide*, $[Ni(NO_2)(MeOH)_2(OH)]$. It was found that refluxing nitrosylamminehydroxymethoxynickel hydroxide in methanol gave a green insoluble product. The infrared spectrum showed the presence of OH and co-ordinated bridging NO_2 groups, as in $[Ni(NO_2)(MeOH)_2(OMe)]_x$.[7] There were no peaks in the nitrosyl region. The structure (I) is probably analogous to that of $[Ni(NO_2)(MeOH)_2(OMe)]_x$ (II):



(I)



(II)

and, in both cases, further polymerisation probably occurs through methoxy- or hydroxy-groups to give six-co-ordinate nickel.

(D) *The Co-ordinated* NO^- *Group*.—Since several of the metal complexes described in this paper could have been formulated with co-ordinated NO^-, we have considered it desirable to confirm the infrared criterion for detecting such a group: namely, a moderately strong band in the region 1045—1200 cm.$^{-1}$ which we have already discussed in connection with the red cobalt nitrosopentammines $[Co(NH_3)_5NO]X_2$ and $K_3[Co(CN)_5NO]$.[8,12] We

[23] Katzin, *Nature*, 1958, **182**, 1013.

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have assigned frequencies of 1045 and 1150 cm.$^{-1}$, respectively, to the stretching mode of the NO^{+} ligand in $[Co(NH_3)_5NO](NO_3)_2$ and $K_3[Co(CN)_5NO]$.[12] However, in a recent study of amminecobalt complexes, including the red nitrosopentammines, by Quagliano and his colleagues [26] it was suggested that N–H vibrations were responsible for these frequencies and that the N–O stretching vibration was at 1620 cm.$^{-1}$. Whilst in our opinion the occurrence of absorption at *ca.* 1100 cm.$^{-1}$ by other complexes not containing ammonia, *e.g.*, $K_3[Co(CN)_5NO]$ and $[Fe(NO)_3NO]$,[12,32] is clear evidence for a stretching frequency associated with the NO^{+} group, we have felt it necessary to confirm our original assignment in the ammine and cyano-salts by using isotopic substitution of the NO group. The observed and the calculated frequencies are recorded in Table 5. The proportion of ^{15}NO in the nitric oxide was estimated by infrared spectroscopy as 61 ± 5% of the total.

TABLE 5. *Infrared spectra (in cm.$^{-1}$) in* NO^{+} *complexes with isotopic replacement.*

Complex	$[Co(NH_3)_5NO](NO_3)_2$	$K_3[Co(CN)_5NO]$
Strong bands in ^{14}NO complex	1610, 1300, 1045, 930, 820	2141, 2104sh, 1150
Strong bands in ^{15}N-enriched complex...	1610, 1300, 1045, 1017, 930, 820	2141, 2104sh, 1150, 1119
Separation of NO– bands	28	31
Calculated separation of NO^{+} bands [higher frequency $(1 - \sqrt{14/15})$]	27	30
Ratio of intensities of peak in doublet (^{15}NO/total) (as %)	56 ± 5	58 ± 5

It is thus clear that the bands in the 1100 cm.$^{-1}$ region in the red nitrosopentammines and in the cyanide complex arise from the NO^{+} group and not from ammine deformation frequencies. The band at 1620 cm.$^{-1}$ assigned by Quagliano and his colleagues to the N–O stretch did not shift in the enriched compounds, and must clearly be an N–H bending mode.

We finally note, in connexion with the cobalt complexes, that aqueous solutions of the red nitrate and of the nitrosyl cyanide have conductivities indicating that they are respectively 2 : 1 and 3 : 1 complexes. (Molar conductivities in water = 251 and 344 ohm^{-1} cm.^{2}, respectively.)

EXPERIMENTAL

Microanalyses and molecular weights are by the Microanalytical Laboratory, Imperial College.

Potassium Nitrosylpentachloroplatinate(II), $K_2[Pt(NO)Cl_5]$.—A suspension of potassium chloroplatinate(II) (2 g.) was shaken with a saturated solution of nitrosyl chloride in anhydrous chloroform (200 ml.) for 24 hr. The green unstable *complex* (2 g., 95%) was removed by filtration and dried *in vacuo* {Found: K, 16·0; N, 2·8; Cl, 37·5. $K_2[Pt(NO)Cl_5]$ requires K, 16·25; N, 2·9; Cl, 36·8%}.

Tetramminenitrosylchloroplatinum(II) *Dichloride*, $[Pt(NO)(NH_3)_4Cl]Cl_2$.—(*a*) This complex was prepared by Jensen's method [3] from tetrammineplatinum(II) chloride in hydrochloric acid solution with nitric oxide {Found: Pt, 48·5; Cl, 26·3; N, 17·2. Calc. for $[Pt(NO)(NH_3)_4Cl]Cl_2$: Pt, 48·8; Cl, 26·6; N, 17·5%}. Molar conductivity in water = 294 ohm^{-1} cm.^{2}.

(*b*) Tetrammineplatinum(II) chloride (2 g.) was suspended in a saturated solution of nitrosyl chloride in chloroform (200 ml.) and shaken for 24 hr. The green, stable solid was removed by filtration and dried *in vacuo* (yield 2 g., 95%) (Found: Pt, 48·3; N, 17·7; Cl, 26·5%).

Nitrosylbis(ethylenediamine)chloroplatinum(II) *Dichloride*, $[Pt(NO)en_2Cl]Cl_2$.—This salt was prepared as above, but from bis(ethylenediamine)platinum(II) chloride (2 g.). It was green and could not be obtained pure (yield, 2 g., 95%) {Found: C, 10·9; H, 3·2; N, 20·1. Calc. for $[Pt(NO)en_2Cl]Cl_2$: C, 12·2; H, 4·0; N, 21·3%}.

Potassium Nitrosyltetranitrochloroplatinate(II), $K_2[Pt(NO)(NO_2)_4Cl]$.—Potassium tetranitroplatinate(II) (2 g.) was shaken with a saturated solution of nitrosyl chloride in chloroform (200 ml.) for 24 hr. The *product* (2 g., 95%) was green {Found: K, 15·3; Pt, 37·4; N, 13·4. $K_2[Pt(NO)(NO_2)_4Cl]$ requires K, 15·0; Pt, 37·3; N, 14·3%}.

Dipyridinonitrochloroplatinum(II), $[Pt\,py_2(NO_2)Cl]$.—Potassium chloroplatinate(II) (2 g.) in water (20 ml.) was shaken for 24 hr. in a slow current of nitric oxide, and pyridine was then added in excess. The yellow precipitate was filtered off, washed with water, alcohol, and

ether, and dried *in vacuo* (yield, 1·5 g., 75%) {Found: Pt, 44·5; N, 9·6; Cl, 27·6; H, 2·4. Calc. for $[Ptpy_2(NO_2)Cl]$: Pt, 44·9; N, 9·7; C, 27·6; H, 2·3%}.

Pyridinium Chloroplatinate(II), $(pyH)_2[PtCl_4],4H_2O$.—The complex $[Ptpy_2(NO_2)Cl]$ (1 g.) was heated for 4 hr. with 17% hydrochloric acid on the steam-bath. The yellow crystalline product was filtered off, washed with water and alcohol, and dried *in vacuo* {Found: Pt, 34·5; C, 21·6; N, 5·3. Calc. for $(pyH)_2[PtCl_4],4H_2O$: Pt, 34·6; C, 21·9; N, 5·1%}.

Nitrosyltetrammineacetatoplatinum(II) *Chloride*, $[Pt(NO)(NH_3)_4OAc]Cl_2$.—Tetrammineplatinum(II) chloride (2 g.) was dissolved in 50% acetic acid (70 ml.) and kept saturated with nitric oxide for 4 hr. The green solid *complex* was filtered off and washed with water, alcohol, and ether (yield, 0·7 g., 30%) {Found: Pt, 42·7; C, 4·7; H, 3·7. $[Pt(NO)(NH_3)_4OAc]Cl_2$ requires Pt, 42·4; C, 5·2; H, 3·8%}.

Nitrosyltetramminenitratoplatinum(II) *Nitrate Chloride*, $[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$.—Tetrammineplatinum(II) chloride (2 g.) was dissolved in 8N-nitric acid (80 ml.) and kept saturated with nitric oxide for 6 hr. The bright green solid *complex* (0·5 g., 20%) was filtered off and washed with alcohol and ether, and dried *in vacuo* {Found: Pt, 43·5; Cl, 8·6; N, 21·6. $[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$ requires Pt, 44·1; Cl, 7·9; N, 21·7%}.

Potassium Nitrosyltetranitronitratoplatinate(II), $K_2[Pt(NO)(NO_2)_4(NO_3)],2H_2O$.—Potassium-tetranitroplatinate(II) (2 g.), was treated with 8N-nitric acid (80 ml.), and the blue solution heated for 4 hr. on the steam-bath. The yellow residue of *complex* (0·6 g., 25%) was recrystallised from 0·1N-nitric acid {Found: K, 13·7; Pt, 33·5; N, 13·1. $K_2[Pt(NO)(NO_2)_4(NO_3)],2H_2O$ requires K, 13·1; Pt, 33·4; N, 13·9%}. Molar conductivity in water = 252 ohm^{-1} $cm.^2$.

Diammineplatinum(IV) *Tetrachloride*, $[Pt(NH_3)_2Cl_4],H_2O$.—Diammineplatinum(II) dinitrite (1 g.) was treated with an excess of 6N-hydrochloric acid for 2 hr. at 80°. The yellow precipitate (0·5 g., 45%) was filtered off, washed with water, alcohol, and ether, and dried *in vacuo* {Found: Pt, 50·7; Cl, 37·1. Calc. for $[Pt(NH_3)_2Cl_4],H_2O$: Pt, 50·2; Cl, 36·5%}.

Tetramminesulphatoplatinum(IV) *Dichloride*, $[Pt(NH_3)_4SO_4]Cl_2$.—Nitrosyltetramminechloroplatinum(II) chloride (2 g.) was treated with 50% sulphuric acid (50 ml.) at 90° for 3 hr. Bright red crystals of the *complex*, which was sparingly soluble in water, were filtered off, washed with water, alcohol, and ether, and dried *in vacuo* (yield, 1 g., 40%) {Found: Pt, 40·5; N, 11·2. $[Pt(NH_3)_4SO_4]Cl_2$ requires Pt, 40·7; N, 11·7}.

Potassium Nitrosyltetranitronitratopalladate(II), $K_2[Pd(NO)(NO_2)_4(NO_3)],2H_2O$.—Potassium tetranitropalladate (2 g.) was treated with 8N-nitric acid at 80° for 2 hr. The red *product* (1 g., 25%) was recrystallised from 0·1N-nitric acid {Found: K, 15·5; Pd, 22·5; N, 16·1. $K_2[Pd(NO)(NO_2)_4(NO_3)],2H_2O$ requires K, 15·5; Pd, 22·0; N, 16·7%}.

Nitrosyldiamminehydroxynickel(II) *Dihydroxide*, $[Ni(NO)(NH_3)_2(OH)](OH)_2$.—A mixture of ammonia and nitric oxide gases (supplied from cylinders and dried) was passed into a solution of nickel carbonyl (5 ml.) in ether (100 ml.) for 3 hr. The blue solid complex (0·5 g., 10%) thus formed was filtered off, washed, and dried *in vacuo* {Found: Ni, 32·2; N, 23·7. Calc. for $[Ni(NO)(NH_3)_2(OH)](OH)_2$: Ni, 33·8; N, 24·2%}. $\chi_A = 3{\cdot}08 \times 10^{-3}$ c.g.s.u. at 295° K.

Nitrosylamminehydroxymethoxynickel(II) *Hydroxide*, $[Ni(NO)(NH_3)(OMe)(OH)](OH)$.—A mixture of ammonia and nitric oxide gases was passed into a solution of nickel carbonyl (5 ml.) in methanol (120 ml.) for 3 hr. The blue *product* (0·5 g., 9%) crystallised from methanol {Found: C, 7·7; H, 3·9; N, 15·7. $[Ni(NO)(NH_3)(OMe)(OH)](OH)$ requires C, 7·1; H, 4·7; N, 16·4%}.

μμ′-*Dinitrodimethanolatedinickel*(II) *Dihydroxide*, $[Ni(NO_2)(OH)(MeOH)]_2,2H_2O$.—The above described nitrosyl complex (2 g.) was refluxed for 6 hr. with 97% methanol under nitrogen. The green, insoluble *product* (1·8 g., 90%) was filtered off, washed with methanol and alcohol, and dried *in vacuo* {Found: C, 7·3; H, 3·9; N, 7·4. $[Ni(NO_2)(OH)(MeOH)]_2,2H_2O$ requires C, 7·0; H, 4·1; N, 8·1%}.

Other Preparations.—The complexes $[Co(NH_3)_5NO](NO_3)_2$ and $K_2[Co(CN)_5NO]$ were made in the known manner.[13] [^{15}N]Nitric oxide was obtained by warming a mixture of enriched potassium nitrite with potassium iodide and sulphuric acid.[29]

Potassium tetranitroplatinate(II) and tetranitropalladate(II) were made by the recorded methods,[25,28] as were tetrammineplatinum(II) chloride and di(ethylenediamine)platinum(II)

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[27] Nast and Rohmer, *Z. anorg. Chem.*, 1956, **285**, 271.
[28] Pezzi-Escot and Couquet, *Compt. rend.*, 1900, **130**, 1073.
[29] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, 1954, p. 233.

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chloride.[30] Nitrosyl chloride was prepared from nitrosylsulphuric acid and sodium chloride, and was purified by redistillation.[31]

Physical Measurements.—Infrared spectra were measured on a Perkin–Elmer recording spectrophotometer, model 21, with sodium chloride optics; absorption spectra were measured on a Perkin–Elmer Spectracord, model 4000, with 1-cm. silica cells.

Polarographic measurements were made with a Tinsley model 19 recording instrument ($m^{\frac{2}{3}}t^{\frac{1}{6}} = 2{\cdot}3$); magnetic measurements at room temperatures were made by the Gouy method with a permanent field of 6500 gauss; those over a temperature range were measured at a field of 5100 gauss.

We thank Johnson, Matthey and Co. Ltd. for the loan of platinum and palladium compounds, the Mond Nickel Co. for nickel carbonyl, and Albright and Wilson (Mfg.) Ltd. for triphenylphosphine. We further thank the Department of Scientific and Industrial Research for a research studentship (W. P. G.) and the Hercules Powder Co. for research expenses.

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169. *Competitive Oxidations. Part II.* The Lower Alkanes and Cyclopropane.*

By W. E. Falconer, J. H. Knox, and A. F. Trotman-Dickenson.

The oxidation of binary mixtures containing methane, ethane, propane, cyclopropane, isobutane, and neopentane has been studied. The relative rates of removal of the hydrocarbons have been measured by gas-chromatography. The relative reactivites of different C–H bonds have been derived. Previous work is discussed, and the nature of the chain-carrying radicals considered.

Studies in oxidation of hydrocarbons ranging from the measurement of knock ratings to that of the rates of slow oxidation emphasise the important effect of structure. Cullis, Hinshelwood, and Mulcahy [1] measured such differences roughly by determining the rates of pressure rise in the oxidation of pairs of hydrocarbons under the same conditions. They recognised that differences in overall reactivity probably resulted from the combined effects of several processes, such as chain initiation, chain propagation, and chain branching. The detailed investigation of these component reactions is clearly important in elucidating the general mechanism of oxidation of hydrocarbons. In this work we have attempted to measure the relative rates of the chain-propagating reactions for a number of hydrocarbons.

The first products of oxidation of a hydrocarbon are likely to be alkyl radicals containing the same number of carbon atoms as the parent hydrocarbon. For most hydrocarbons there will be more than one such radical. These radicals can either decompose or react with oxygen, and their rates of formation can be found by determining the yields of products which are characteristic of the radicals initially formed. This approach has been used by Burt, Cullis, Larsen, and Minkoff,[2] and by Cullis, Hardy, and Turner.[3]

* Part I, Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509.

[1] Cullis and Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 117; Mulcahy, *ibid.*, p. 128.
[2] Burt, Ebeid, and Minkoff, *Nature*, 1957, **180**, 188; Burt, Cullis, Larsen, and Minkoff, Seventh Symposium on Combustion, Butterworths, London, 1959, p. 428.
[3] Cullis, Hardy, and Turner, *Proc. Roy. Soc.*, 1958, *A*, **244**, 573; 1959, *A*, **251**, 265.

The former measured the relative yields of OH and OD in the products from the oxidation of a number of deuteropropanes at 423°, using infrared spectroscopy. They found that the chance of a given secondary hydrogen atom's appearing in the products as OH was about twice that of a given primary hydrogen atom so appearing. They argued that initial attack at a given secondary C–H bond was twice as fast as initial attack at a primary C–H bond. Since water and hydrogen peroxide are the main hydroxyl-containing products their conclusion requires that both the hydrogen atoms in these products arise from the initial removal of hydrogen from propane. It is impossible to devise a plausible mechanism for which this is true. If one accepts the HO_2 chain mechanism for the high-temperature oxidation of propane,[4,5] the water and hydrogen peroxide should contain equal quantities of primary and secondary hydrogen atoms: the chance that a given secondary atom appears in the water is thus three times the chance that a given primary hydrogen atom so appears. The value obtained by Burt *et al.* is not far from this, but it indicates that considerable secondary oxidation must have taken place and that, in the later stages, oxidation to water of the hydrogen initially on primary carbon atoms predominates. The results give no information about the relative rates of initial attack at different positions in the propane molecule.

Cullis, Hardy, and Turner [3] determined the points of origin of the carbon in carbon monoxide and carbonyl groups formed in the oxidation of ^{14}C-labelled 2-methylpentanes (isohexane) at 242° and assumed that the relative yields gave the relative rates of initial attack at different points in isohexane. They assumed that all alkyl radicals initially formed gave rise to the appropriate hydroperoxide, and that in the subsequent reactions of the hydroperoxide the C–O bond remained unbroken. They also assumed that primary and secondary hydroperoxides gave carbon monoxide in the same proportion and that the tertiary hydroperoxide gave equal molar yield of (carbon monoxide + carbonyl compounds). Kirk and Knox [6] have shown that carbon monoxide arises in roughly equal yields (about 10%) on heterogeneous decomposition of ethyl, isopropyl, and t-butyl hydroperoxides. Carbonyl compounds are formed as a result of the homogeneous decomposition from pyrolysis of alkoxy-radicals. There is no reason to believe that the carbon in the carbon monoxide was that originally attached to the oxygen in the hydroperoxide, and one cannot add the yield of carbon monoxide to the yield of carbonyl to obtain the original amount of hydroperoxide. While it is conceivable that the yields of carbon monoxide may give a measure of the initial attack on the isohexane molecule, we do not as yet known enough about the mechanism of the oxidation at 242° to justify this conclusion.

There is therefore no reliable information about the relative rates of initial attack at different points in a given hydrocarbon undergoing oxidation in the gas phase.

Knox, Smith, and Trotman-Dickenson [7] estimated the rates of attack at different points in hydrocarbons from measurements of the rates of consumption of hydrocarbons in binary mixtures.

If two hydrocarbons R^1H and R^2H form alkyl radicals R^1 and R^2, and if these radicals eventually produce oxygenated radicals X^1 and X^2 which then attack the hydrocarbons, we can write four propagating reactions which remove the hydrocarbons:

$$X^1 + R^1H = X^1H + R^1 \qquad k_{11}$$
$$X^2 + R^2H = X^2H + R^2 \qquad k_{22}$$
$$X^2 + R^1H = X^2H + R^1 \qquad k_{12}$$
$$X^1 + R^2H = X^1H + R^2 \qquad k_{21}$$

[4] Falconer and Knox, *Proc. Roy. Soc.*, 1959, *A*, **250**, 493.
[5] Satterfield and Wilson, *Ind. Eng. Chem.*, 1954, **46**, 1001.
[6] Kirk and Knox, *Trans. Faraday Soc.*, 1960, **56**, 1296.
[7] Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509; Seventh Symposium on Combustion, Butterworths, London, 1959, p. 126.

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Experimentally we measure the relative rates of removal of the two hydrocarbons and obtain an experimental rate constant ratio given by

$$\frac{k_1}{k_2} = \frac{\log \{[R^1H]_{initial}/[R^1H]_{final}\}}{\log \{[R^2H]_{initial}/[R^2H]_{final}\}}$$

If $k_{11} \neq k_{12}$ and $k_{22} \neq k_{21}$ the experimental ratio k_1/k_2 will depend upon the composition of the mixture. The original work on propane–ethane and propane–isobutane mixtures showed that k_1/k_2 was independent of $[R^1H]/[R^2H]$, independent of $[O_2]$/[total RH] with less than 33% of oxygen, and independent of temperature from 274° to 495°. The present work, which uses the same experimental technique, has substantiated the findings of the earlier work but has revealed a dependence of k_1/k_2 upon oxygen concentration in mixtures containing more than 33% of oxygen.

Results

Methane–Ethane.—The oxidation of methane–ethane mixtures was studied only at 495° since the rate of oxidation at lower temperatures was very low at accessible pressures. The study was complicated because methane is an important product of the oxidation of ethane, and in certain instances so much methane was thus formed that the methane content of the mixture actually increased. In order to minimise the effect of the methane formed from ethane, all mixtures studied contained at least as much methane as ethane. Studies of the oxidation of ethane alone showed that with oxygen pressures below about 100 mm. the methane yield was 16 ± 2% of the ethane initially present (see Table 1). At higher oxygen pressures, the yield of methane was dependent on pressure in mixtures of given $[O_2]/[C_2H_6]$ ratio falling to a minimum value of about 2% at high pressures. Addition of nitrogen had no significant effect. In view of this, experiments were carried out only under conditions where a 16% yield of methane was

Table 1. *Oxidation of ethane at* 495°.

No. of expts.	$[O_2]/[C_2H_6]$	$[N_2]$ total press.	Total press. (mm.)	C_2H_4/C_2H_6 (cons.) *	$100CH_4/C_2H_6$ (cons.) *
5	0·25	Nil	100—360	0·64	15 ± 2
5	0·48	0·32	110—400	0·59	17 ± 2
5	0·72	Nil	105—300	0·48	18 ± 2
1	1·50	,,	108	0·28	15·6
1	,,	,,	149	—	15·4
1	,,	,,	165	0·26	15·2
1	,,	,,	179	0·13	7·5 †
1	,,	,,	201	0·03	6·6 †
1	,,	,,	250	0·01	1·7 †
1	,,	,,	288	0·01	1·5 †
1	1·93	0·33	96	0·20	15·0
1	,,	,,	153	0·20	13·2
1	,,	,,	204	0·20	11·3
1	,,	,,	272	0·00	1·9 †
1	,,	,,	355	0·01	0·4 †

* C_2H_6 (cons.) is the amount of ethane consumed in a run.

† These values are not included in the average value used as a correction factor in calculating k(methane)/k(ethane).

to be expected. An appropriate correction to the methane concentration was made in calculating k(methane)/k(ethane). The reproducibility of this ratio at constant oxygen concentration when $[CH_4]/[C_2H_6]$ varies between 4 : 1 and 1 : 1 is evidence for the validity of the practice.

The relative rate of consumption of methane and ethane under these conditions is strongly dependent upon $[O_2]$/[RH], but independent of the total pressure in a mixture of given composition (see Table 2 and Fig. 1).

Preliminary study of the oxidation of ethane alone showed that ethylene was a major product. The conversion of ethane into ethylene was almost independent of pressure for a given value of $[O_2]/[C_2H_6]$ with $[O_2]$ below 100 mm., but fell at higher oxygen pressures. The

variation of the low-pressure conversion into ethylene with $[O_2]/[C_2H_6]$ is shown in Fig. 2. Extrapolation to zero $[O_2]/[C_2H_6]$ shows that in oxygen-weak mixtures about 80% of the ethane removed is converted into ethylene. This value is in general agreement with the known yields of olefins obtained in other high-temperature oxidations (*e.g.*, of propane; Satterfield and

TABLE 2. *Oxidation of methane–ethane mixtures at* 495°.

No. of expts.	Press. range (mm.)	$\frac{[CH_4]}{[C_2H_6]}$	$\frac{[Oxygen]}{[Hydrocarbon]}$	$\frac{k(CH_4)}{k(C_2H_6)}$	No. of expts.	Press. range (mm.)	$\frac{[CH_4]}{[C_2H_6]}$	$\frac{[Oxygen]}{[Hydrocarbon]}$	$\frac{k(CH_4)}{k(C_2H_6)}$
4	188—363	2·0	0·26	0·07	2	187—327	2·0	0·96	0·19
5	211—353	2·0	0·38	0·08	3	237—318	4·0	1·03	0·20
6	111—352	2·0	0·49	0·12	4	153—290	2·0	1·05	0·19
3	255—339	4·0	0·50	0·13	3	203—303	2·0	1·90	0·36
6	133—422	1·0	0·55	0·13					

Wilson,[5] Falconer and Knox [4]). It also agrees with a figure obtained by Knox and Wells [3] for the initial conversion of ethane into ethylene at 360°. When $[O_2]$ exceeded 100 mm., the conversion into ethylene fell sharply with pressure. The ethylene yield was low when the amount of residual methane was also low.

FIG. 1. *Variation of the relative rates of oxidation with* $[O_2]/[RH]$. k(cyclopropane)/k(ethane) (○, ●, ◑); k(methane)/k(ethane) (+).

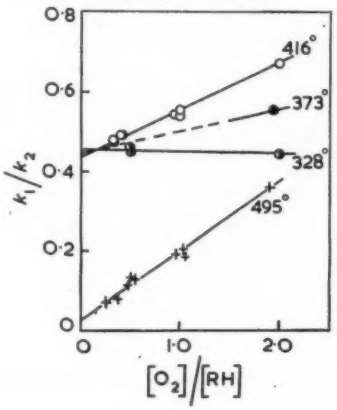
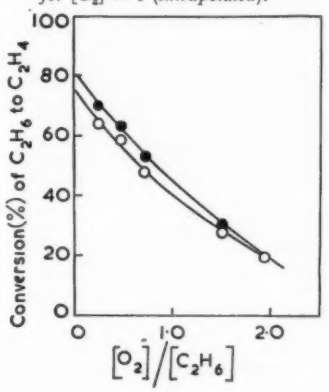


FIG. 2. *Dependence of the conversion of ethane into ethylene at* 495° *upon* $[O_2]/[C_2H_6]$. ○ *Average values for* $[O_2] = 100$ *mm.* ● *Values for* $[O_2] = 0$ *(extrapolated).*



Cyclopropane–Ethane.—The oxidation of this mixture is complicated by the possible isomerisation of cyclopropane to propene at higher temperatures. Below 416° less than 1% of the cyclopropane isomerised during a run. The relative rates of consumption were independent of $[O_2]/[RH]$ at 328° but increased markedly at 416° (Table 3, Fig. 1). The value (0·45) of k(cyclopropane)/k(ethane) at zero $[O_2]/[RH]$ is independent of temperature from 328° to 416°.

Ethylene was again a major product. The ethylene conversions for $[O_2]/[RH] = 0$ rose from about 60% at 328° to nearly 100% at 416°.

Ethane–Neopentane.—Neopentane is a particularly interesting hydrocarbon from the point of view of oxidation since no pentene can be formed from it by an HO_2 radical chain. Oxidation of neopentane might therefore involve radicals different from those taking part in the oxidations of other hydrocarbons, and there might be a strong dependence of the relative rates of removal on [Neopentane]/[Ethane]. Variation of this ratio over a six-fold range at 421° (Table 4) showed that this is not the case. The rate of removal of ethane relative to neopentane is independent of $[O_2]/[RH]$ at the lowest temperature (328°) but increases with $[O_2]/[RH]$ at

[3] Knox and Wells, unpublished results.

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higher temperatures (Fig. 3). Whereas in the oxidations of methane–ethane and cyclopropane–ethane mixtures the ethane becomes relatively less reactive as $[O_2]/[RH]$ is increased, it becomes relatively more reactive in ethane–neopentane mixtures. For $[O_2]/[RH] = 0$, the relative rates of removal are given by:

$$k(\text{ethane})/k(\text{neopentane}) = 0{\cdot}14 \exp(1600/\boldsymbol{R}T)$$

A brief study of the oxidation of neopentane alone at 495° showed that although no pentene was formed, isobutene was a major product. It is presumably formed by the pyrolysis of the neopentyl radical: $\cdot CH_2 \cdot CMe_3 \longrightarrow CH_2{:}CMe_2 + Me\cdot$. In the competitive oxidations, the proportion of neopentane converted into isobutene increases with temperature, probably

TABLE 3. *Oxidation of cyclopropane–ethane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_6]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_6)}{k(C_2H_6)}$	No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_6]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_6)}{k(C_2H_6)}$
3	328°	200—390	2·0	0·49	0·46	8	416°	79—403	3·0	0·50	0·49
8	328	104—360	0·5	0·50	0·45	4	416	114—405	0·33	0·51	0·49
9	328	110—442	1·0	2·00	0·44	2	416	188—325	1·0	0·95	0·54
						5	416	89—430	3·0	1·00	0·54
3	373	176—245	2·0	1·96	0·55	7	416	85—437	0·33	1·00	0·55
						6	416	260—456	1·0	2·00	0·67
4	416	98—355	0·33	0·33	0·48						
5	416	85—293	3·0	0·35	0·47						

TABLE 4. *Oxidation of ethane–neopentane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_2H_6]}{[C_5H_{12}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_2H_6)}{k(C_5H_{12})}$	No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_2H_6]}{[C_5H_{12}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_2H_6}{k(C_5H_{12})}$
3	328°	230—320	1·0	0·33	0·53	5	421°	185—425	2·0	1·22	0·54
4	328	180—330	2·0	0·64	0·51	4	421	210—310	0·5	1·26	0·53
5	328	245—390	2·0	1·50	0·54	4	421	180—340	2·0	2·00	0·59
3	328	270—405	2·0	2·96	0·54	5	421	250—390	2·0	2·92	0·73
5	421	180—330	2·0	0·25	0·47	3	495	210—370	2·0	0·25	0·40
4	421	205—320	0·5	0·25	0·48	3	495	160—315	0·5	0·50	0·46
6	421	160—300	1·0	0·50	0·48	3	495	225—365	2·0	0·50	0·43
7	421	170—405	3·0	0·50	0·49	3	495	175—290	2·0	1·00	0·51
5	421	130—380	0·5	0·50	0·48	3	495	225—290	2·0	2·06	0·66
5	421	200—400	2·0	0·82	0·51						

because the decomposition of the neopentyl radical has a higher activation energy than its oxidation.

Neopentane–Isobutane.—Only 1 : 1 mixtures were investigated (Table 5). At 326° there was no dependence upon $[O_2]/[RH]$, but at higher temperatures the neopentane became relatively more reactive as $[O_2]/[RH]$ was increased (Fig. 3). For $[O_2]/[RH] = 0$, the relative rates of oxidation are given by:

$$k(\text{neopentane})/k(\text{isobutane}) = 0{\cdot}26 \exp(1000/\boldsymbol{R}T)$$

for the range 328—495°. Isobutene is a major product of the oxidation of both isobutane and neopentane.

The oxygen-dependence for this and the previous mixture indicates that there should be a strong oxygen-dependence in the ethane–isobutane oxidation.

Propane–Isobutane.—The results of a number of experiments carried out by Smith on this mixture are recorded in Table 6. The range of oxygen concentration is too small to disclose any dependence upon $[O_2]/[RH]$. The mean value of $k(\text{propane})/k(\text{isobutane})$ between 310° and 420° is 0·67.

Ethane–Propane.—This system was extensively studied by Knox, Smith, and Trotman-Dickenson [7] with mixtures in which $[O_2]/[RH]$ was less than 0·50. In this region no dependence upon $[O_2]/[RH]$ was noted. A few experiments with much higher $[O_2]/[RH]$ ratios summarised

TABLE 5. *Oxidation of neopentane–isobutane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_5H_{12}]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_5H_{12})}{k(C_4H_{10})}$	No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_5H_{12}]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_5H_{12})}{k(C_4H_{10})}$
2	326°	255—365	1·0	0·52	0·61	2	492°	265—295	1·0	0·33	0·57
2	326	235—295	1·0	1·50	0·63	2	492	160—180	1·0	1·00	0·66
						2	492	165—180	1·0	2·00	0·69
2	421	195—330	1·0	0·35	0·59						
2	421	275—345	1·0	1·00	0·68						
2	421	270—285	1·0	2·45	0·73						

TABLE 6. *Oxidation of propane–isobutane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_8]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_8)}{k(C_4H_{10})}$	No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_8]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_8)}{k(C_4H_{10})}$
5	310°	140—420	1·0	0·50	0·66	3	420°	170—400	1·0	0·50	0·60
4	310	180—315	3·0	0·50	0·70	2	420	155—245	0·33	0·50	0·73
3	420	145—335	0·33	0·40	0·68	3	420	155—345	3·0	0·75	0·68

in Table 7, show that the dependence upon $[O_2]/[RH]$ is comparable with that in the neopentane–ethane system. The ethane appears more reactive as $[O_2]/[RH]$ is raised. Thus the relative oxidation rates of propane and neopentane should be nearly independent of $[O_2]/[RH]$.

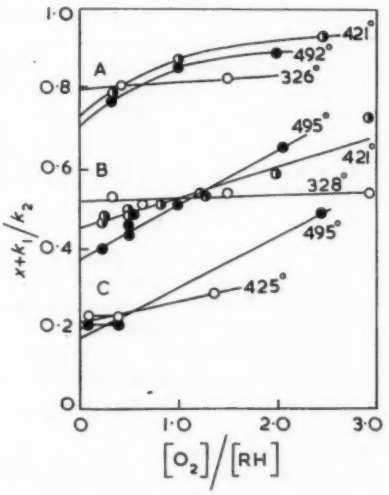

FIG. 3. *Variation of the relative rates of oxidation with* $[O_2]/[RH]$.
(A), k(neopentane)/k(isobutane), $x = 0{\cdot}20$;
(B), k(ethane)/k(neopentane), $x = 0$;
(C), k(ethane)/k(propane), $x = -0{\cdot}20$.

Additives.—One of the most striking effects noted in the present work is the relative independence of the relative rates of oxidation on $[O_2]/[RH]$ at low temperatures and the very marked effect of changes in this ratio at 400° and above. These results can indicate only that the products play an important part in governing the composition of the free-radical mixture which removes the parent hydrocarbons in the later stages of oxidation at higher temperatures. With this in mind, experiments were carried out with ethane–propane mixtures to ascertain whether any of the more probable initial products could account for the change.

The results presented in Table 7 show that addition of ethylene, propene, methanol, or formic acid has no measurable effect at 425°. Hydrogen and formic acid were likewise ineffective at 495°.

Acetaldehyde, normally regarded as a potent accelerator of oxidations, had only a slight effect at 495° and no effect at 425°. At 495°, 10% was required to give a moderate increase in k(ethane)/k(propane). This amount is far in excess of that likely to be present in the oxidations, and its effect is considerably less than that obtained by adding more oxygen. We therefore have no direct experimental evidence as to the cause of the marked dependence of the

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relative oxidation rates on the oxygen to hydrocarbon ratio. It is not caused by the oxidation of any of the products mentioned above.

During the study of the effect of addition of ethylene it was noted that the ethane consumption was sometimes unexpectedly small. This was shown to be due to the formation of saturated hydrocarbons from the last stages of the oxidation of the olefin. As is shown in

TABLE 7. *Effect of additives on ethane–propane oxidations at* 425° *and* 495°.

No. of expts.	Additive	[Oxygen]/[Hydrocarbon]	Temp. (°c)	$k(C_2H_6)/k(C_3H_8)$
—	None	<0·50	425°	0·43 [7]
2	None	1·35	425	0·49
3	40% C_2H_4	0·25	425	0·45
2	50% C_2H_4	0·25	425	0·43
2	23% C_2H_4	1·35	425	0·51
3	23% C_2H_6	0·50	425	0·43
3	26% CH_3·OH	0·47	425	0·41
3	6% H·CO_2H	0·57	425	0·45
—	None	<0·50	495	0·41 [7]
1	None	0·34	495	0·41
2	None	2·45	495	0·79
2	2% CH_3·CHO	0·34	495°	0·45
2	11% CH_3·CHO	0·50	495	0·54
2	25% CH_3·CHO	0·33	495	0·53
2	10% CH_3·CHO + 10% C_2H_4	0·42	495	0·52
2	10% CH_3·CHO + 10% C_2H_6	0·41	495	0·51
1	6% H·CO_2H	0·42	495	0·39
2	19% H_2	0·34	495	0·41

TABLE 8. *Oxidation of olefins at* 425° *and* 495°.

Olefin	[Oxygen]/[Olefin]	Extent of reaction	Temp. (°c)	100 C_2H_6 / Olefin (cons.) *	100 C_3H_8 / C_3H_6 (cons.)
C_2H_4	0·50	Complete	425°	8	—
	0·50	2/3 complete	425	0	—
	0·50	Complete	495	11	—
	0·50	2/3 complete	495	2	—
C_3H_6	0·50	Complete	425	2·5	3·5
	0·50	2/3 complete	425	0	0

* Olefin (cons.) is the amount of olefin consumed in a run.

Table 8, up to 11% of the ethylene can be converted into ethane during the later stages of its oxidation at high temperatures. If, however, the reaction mixture is removed from the reaction vessel before the oxygen is exhausted, the conversion into saturated hydrocarbon is greatly reduced. With propene, both ethane and propane are formed. It is clear, therefore, that transfer of hydrogen to the olefin occurs, and that this is followed by abstraction of a hydrogen atom by the alkyl radical thereby formed. A suggested reaction is:

$$C_2H_4 + HO_2 = C_2H_5 + O_2$$

Hydrogen abstraction will only occur when the oxygen concentration is very low. Alternatively, two alkyl radicals can disproportionate to form molecules of alkane and olefin.

DISCUSSION

The main experimental findings may be summarised as follows: (1) All the oxidations studied show the same basic features. (2) The overall relative rate constants k_1/k_2 do not depend upon $[R^1H]/[R^2H]$. (3) The ratios k_1/k_2 are independent of $[O_2]/[RH]$ at 328°, but are dependent on it at temperatures above 400°. As $[O_2]/[RH]$ increases the values tend to unity. (4) The temperature variations of k_1/k_2 at zero $[O_2]/[RH]$ are slight. The largest temperature effect was for the ethane–neopentane mixture, for which the activation energy difference was about 1·6 kcal. mole^{-1}. (5) While the overall rates of oxidation of hydrocarbons differ greatly, the relative rates of oxidation in mixtures studied differ by factors of not more than 2 in all cases except methane–ethane.

The independence of the relative rate constants on $[R^1H]/[R^2H]$ indicates that the reactivities of the propagating radicals derived from different hydrocarbons are identical. In terms of the mechanism given in the introduction, $k_{11} = k_{12}$, and $k_{22} = k_{21}$. This applies

over the whole temperature range and at all ratios of oxygen to hydrocarbon, even when the value of k_1/k_2 depends upon $[O_2]/[RH]$.

TABLE 9. *Relative reactivites of saturated hydrocarbons.*

Attacking radical:	F	Cl	Oxid.*	CF_3	MeO	CH_3	Br
Methane	0·6	0·02	0·03	0·05	—	0·03	0·002
Ethane	1	1	1	1	1	1	1
Propane	1·4	2·0	2·3	3·0	3·3	3·3	43
Cyclopropane	0·9	0·03	0·45	—	0·3	0·55	—
Isobutane	1·7	2·0	3·6	7·5	5·3	10	1050
Neopentane	1·8	2·1	2·0	1·5	1·5	1·7	0·75
Temp.	25°	250°	350°	182°	250°	182°	98°
Ref.	12	10	7	15	11	14	13

* " Oxid." refers to the chain-carrying radical in oxidations when $[O_2]/[RH] = 0$.

It has been shown [4,9] that variation of the oxygen concentration in the oxidation of propane between 320° and 480° has little effect upon the yields of the major products formed in the initial stages of reaction. The effect of oxygen is basically to increase the extent of reaction and thereby to alter the nature of the final products. The effect of $[O_2]/[RH]$ on k_1/k_2 at the higher temperatures does not therefore necessarily reflect any change in the initial rates of removal of the two hydrocarbons. It is more likely that the rates of removal in the later stages of reaction differ. This implies that the nature of the radical or radicals that remove the hydrocarbons changes as the reaction proceeds.

Analytical evidence presented here and elsewhere shows that in the early stages of oxidations the olefins corresponding to the original hydrocarbon are the major initial products. The only chain scheme that satisfactorily explains this is an HO_2 radical chain:

$$\text{Alkyl radical} + O_2 = \text{Olefin} + HO_2$$

$$\text{Alkane} + HO_2 = \text{Alkyl radical} + H_2O_2$$

It therefore seems likely that the values of k_1/k_2 that we have obtained by extrapolation to zero oxygen concentration apply to the HO_2 radical. This could be checked in detail by measurement of the initial olefin yields in competitive oxidations. The relative reactivites obtained (Table 9) may be compared with the relative reactivities of other radicals which have been studied in competitive systems.[10–15] The radical operative in oxidations is of relatively high reactivity, comparable with that of a chlorine atom [10] or a methoxyl radical.[11] The radical is less reactive than a fluorine atom [13] and more reactive than a methyl radical.[14] The identification of the radical in oxidations as HO_2 suffers from the difficulty that the commonly accepted strength [16] of the first O–H bond in hydrogen peroxide is 89·5 kcal., whereas the observed reactivities must be attributed to a radical that forms a bond of about 100 kcal. mole^{-1} with a hydrogen atom.

With chlorine [10] and bromine [12] atoms and with methyl radicals,[14] the reactivity does

[9] Knox, *Trans. Faraday Soc.*, 1960, **56**, 1225.
[10] Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.
[11] Shaw and Trotman-Dickenson, *J.*, 1960, 3210; Berces and Trotman-Dickenson, unpublished results.
[12] Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 1064.
[13] Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469; Anson, Fredricks, and Tedder, *J.*, 1959, 918; Fettis and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1959, **81**, 5260; Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 4177.
[14] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.
[15] Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 103; Ayscough, *J. Chem. Phys.*, 1956, **24**, 944; Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849.
[16] Foner and Hudson, *J. Chem. Phys.*, 1955, **23**, 1364.

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not vary much from one hydrocarbon to another for bonds of a given order. It is therefore reasonable to assume that this holds approximately for the radical involved in oxidations, and hence to derive the relative reactivities in Table 10. Apart from the expected trend in the direction of primary, secondary, and tertiary, it is notable that the CH bond of cyclopropane is about 8 times less reactive than a normal secondary bond, and the CH in methane about 20 times less reactive than a normal primary bond.

The identity of the radical or radicals responsible for the removal of hydrocarbon in the later stages of oxidation is not at all clear. Studies of propane oxidation [4,9] show that a major feature of the oxidation in the later stages is the removal of olefin. It appears that olefins react much faster than saturated hydrocarbons of the same carbon number. It was therefore possible that addition of olefin could induce behaviour characteristic of a mature reaction from the start of an oxidation. The experiments in which ethylene and propene were added to ethane–propane mixtures showed that this was not the case. Even the addition of acetaldehyde had little effect. The product from which the later-stage

TABLE 10. *Relative reactivities of hydrogen atoms.*

	Relative reactivity towards:						
Type of H atom	F	Cl	Oxid.*	CF_3	MeO	CH_3	Br
Methyl	0·8	0·03	0·05	0·08	—	0·04	0·002
Cyclopropyl	0·9	0·03	0·45	—	0·29	0·55	—
Primary	1	1	1	1	1	1	1
Secondary	1·2	3	4	6	8	7	250
Tertiary	1·4	3	11	36	26	50	6300
Temp.	25°	250°	350°	182°	250°	182°	98°
Ref.	12	10	7	15	11	14	13

" Oxid." refers to the chain-carrying radical in oxidations when $[O_2]/[RH] = 0$.

radicals are derived is therefore still uncertain but might be formaldehyde. From the fact that there is no dependence of the k ratio upon the relative concentrations of the two hydrocarbons, we deduce that the important radicals at this stage are not characteristic of the hydrocarbons forming them. Since this applies even to methane–ethane mixtures, it is likely that the radical contains at most one carbon atom. We are therefore limited to OH, CHO, CH_3, CH_3·O, and CH_3·O·O. The absence of methane as a product, except at the very end of the reactions, suggests that methyl radicals are oxidised before they have time to abstract hydrogen. The formation of methanol [17] suggests that methoxyl radicals are present, but the relative reactivities of the hydrocarbons with them,[11] as with methyl radicals,[14] do not correspond to those observed. The low strength of the H–CHO bond eliminates formyl radicals. Alkylperoxy-radicals seem unlikely for several reasons. They would be expected to behave very like hydroperoxy-radicals. They would be expected to be present at low temperatures and should, if they are highly reactive, be the chain carriers. Further, preliminary results indicate that their reactivities do not meet the requirements. Hence we conclude that hydroxyl radicals are the most probable chain carriers responsible for removal of the saturated hydrocarbons in the later stages of the reactions at high temperatures.

EXPERIMENTAL

Materials.—Methane, ethane, cyclopropane, isobutane, and neopentane were obtained from cylinders, thoroughly degassed, and stored in 2-l. bulbs. The ethane used in ethane–cyclopropane and ethane–methane oxidations was passed through a column packed with a mercuric acetate–mercuric nitrate–ethylene glycol solution supported on 20—30-mesh firebrick [18] to remove the ethylene present in the cylinder gas; that used in neopentane–ethane oxidations was freed

[17] Pease, *J. Amer. Chem. Soc.*, 1938, **60**, 2244; Bailey and Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 311; Knox and Norrish, *ibid.*, 1954, *A*, **221**, 151.
[18] Kerr and Trotman-Dickenson, *Nature*, 1958, **182**, 466.

from ethylene by passing it through sulphuric acid and charcoal saturated with bromine. Bromine vapour and bromides were removed by 30% *NN*-dimethyl-*p*-toluidine supported on 40—60-mesh firebrick. Ethylene and propene were free from ethane and propane. Analysis of the hydrocarbons showed them to be better than 99·5% pure. Oxygen was obtained from B.O.G. cylinders. The acetaldehyde used as an initiator was of " AnalaR " quality.

Apparatus and Procedure.—Oxidations were carried out in a conventional static high-vacuum apparatus. The reaction vessel (107 ml.; Pyrex) was enclosed in an electric furnace controlled by a thermostat to $\pm 1°$; the temperature along the length of the reaction vessel was constant within 1°.

The hydrocarbons and oxygen, measured in a constant-volume gas burette, were mixed before each series of runs. Some mixture was allowed to enter the pre-heated reaction vessel, and the initial pressure of the gases was noted on a mercury manometer. The reactions were followed by the pressure rise on the manometer and when this rise had ceased the condensable gases were frozen into a sampling tube at −183° for analysis; the non-condensable gases were pumped off. In order to analyse mixtures containing methane, the sampling tube was packed with activated alumina to condense the methane. Samples were normally withdrawn after the reaction had run to completion. However, k_1/k_2 was independent of the extent of reaction beyond 80%. Small quantities of acetaldehyde introduced as an initiator in some of the low-temperature oxidations of ethane–cyclopropane mixtures had no effect on the observed rate constant ratio.

Analysis.—Analysis was by gas chromatography, carbon dioxide being used as the carrier gas; the gases were determined with a Janak nitrometer.[19]

Ethane, ethylene, and cyclopropane were separated on an 80-cm. column of silver nitrate–ethylene glycol–30—40 mesh firebrick [20] followed by 280 cm. of 40—60-mesh activated alumina poisoned with $\frac{1}{4}$% of squalane.

Methane, ethane, and ethylene were separated with split columns. The first column consisted of 80 cm. of the silver nitrate mixture followed by 160 cm. of poisoned alumina. The second was 240 cm. of Sutcliffe and Speakman's 32—40-mesh activated charcoal. During analysis the two columns were at first connected in series, and the methane and other permanent gases eluted on to the charcoal column and isolated. The ethane and ethylene were then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal column.

For ethane, ethylene, isobutene, and neopentane a three-section column was employed. The first section was 240 cm. of 20% nitrobenzene on 52—72-mesh firebrick; the second, 80 cm. of silver nitrate mixture followed by 160 cm. of poisoned alumina; the third 120 cm. of the silver nitrate mixture. In analysis, sections one and two were first connected in series, and carbon dioxide passed until the ethane and ethylene were isolated on the second section of the column. Sections one and three were then connected in series, and the isobutene and neopentane eluted directly into the detector. Finally, the ethane and ethylene were eluted from section two.

Isobutene, isobutane, neopentane, and the C_3 and C_3 hydrocarbons were separated as follows: The contents of the sample tube were eluted on to a column of 10 cm. of poisoned alumina followed by 230 cm. of 20% nitrobenzene on firebrick, and the C_3 and C_3 hydrocarbons were eluted into the atmosphere. The column was then connected in series with 120 cm. of silver nitrate mixture, and the C_4 and C_5 hydrocarbons were eluted.

All columns were operated at room temperature. Standardisation runs were carried out for each furnace temperature, the normal procedure being used for an oxidation, but with omission of the oxygen from the original mixture. In this way systematic errors of calibration were eliminated. The accuracy of the analytical results was about ± 1%.

This work has been made possible through the support and sponsorship of the U.S. Department of Army, through its European Research Office.

CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY. [*Received, July 25th,* 1960.]

[19] Janak, *Coll. Czech. Chem. Comm.*, 1954, **19**, 684, 917.
[20] Bednas and Russell, *Canad. J. Chem.*, 1958, **36**, 1272.

XUM

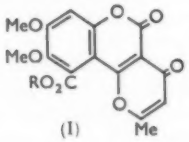
170. *Derivatives of Hydroxyquinol. Part II.*[1] *The Synthesis of 2-Acetyl-4,5,7-trimethoxyindane-1,3-dione: Revised Structures for Some Degradation Products from Citromycetin.*

By F. M. Dean, D. R. Randell, and Graham Winfield.

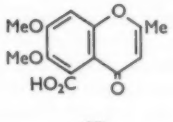
By synthesis of its methyl ether, the degradation product $C_{13}H_{12}O_6$, m. p. 156°, common to both methyl di-*O*-methylanhydrofulvate and methyl di-*O*-methylcitromycetinone, is shown to be 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione. The chief step in this synthesis is an ozonolysis of 3,4,6-trimethoxy-2-propenylacetophenone effected by a novel technique.

The course of alkali-degradation of citromycetinone derivatives is elucidated, and revised structures are offered for several of the products.

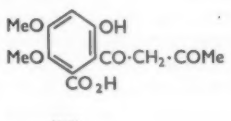
When citromycetin is converted into methyl di-*O*-methylcitromycetinone (I; R = Me) and hydrolysed by aqueous alkali, an acidic substance $C_{11}H_6O_4(OMe)_2$ is formed that was originally allocated [2] structure (II), this being considered to arise by cyclisation of an intermediate (III). From similar hydrolyses Hetherington and Raistrick [3] obtained also another substance $C_{10}H_6O_3(OMe)_3$ which they thought to be a pyrone, possibly (IV): unable to reproduce this result, subsequent workers [4] proved that 3-hydroxy-6,7-dimethoxy-2-methylchromone (IV), obtained synthetically, had properties widely different from those described in the earlier report. Later workers [5] found sodium methoxide to convert methyl di-*O*-methylanhydrofulvate (V) into the acidic substance thought to be (II), but the further examinations made possible by this discovery led to the suggestion that for this compound structure (VI; R = H) was to be preferred to structure (II). This revision is now confirmed by a synthesis of 2-acetyl-4,5,7-trimethoxyindane-1,3-dione identical with the methyl ether of the degradation product.



(I)



(II)



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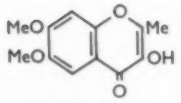

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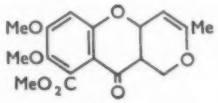

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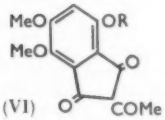


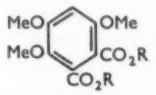
(VI)

Methylation of the degradation product (VI; R = H) gave the ether (VI; R = Me) in accordance with the relative resistance of 2-acetylindane-1,3-dione itself to alkylation. Permanganate oxidation then gave the phthalic acid (VII; R = H), thereby excluding structure (II) but not necessarily proving the correctness of the alternative (VI; R = H).

Though in the past 2-acetylindane-1,3-diones have been made by base-catalysed condensation of alkyl phthalates with acetone, this reaction failed when applied to the phthalate (VII; R = Me). During the exploration of an alternative route it was shown [1] that ozone converts the propenylacetophenone (VIII) into an iso-ozonide so stable that the desired aldehyde could not be obtained from it. Since the last step in the formation of an iso-ozonide is often held to be cyclisation of an intermediate of type (IX), this ozonolysis

[1] Part I, Dean, Randell, and Winfield, *J.*, 1959, 1071.
[2] Robertson, Whalley, and Yates, *J.*, 1951, 2013.
[3] Hetherington and Raistrick, *Phil. Trans.*, 1931, *B*, **220**, 209.
[4] Jones, Mackenzie, Robertson, and Whalley, *J.*, 1949, 562.
[5] Dean, Eade, Moubasher, and Robertson, *J.*, 1957, 3497.

has been re-investigated with the aid of damp ozone so that the water present could compete for the carbonium centre in (IX), promoting fission in the desired direction. This technique gave the aldehyde (X) in good yield along with a little of the stable iso-ozonide. The structure of the aldehyde (X) was confirmed by (*a*) converting it by an internal Cannizzaro reaction into the phthalide (XI), and (*b*) subjecting it to Dakin oxidation. The latter removed the acetyl group selectively, leaving the salicylaldehyde (XII) which condensed with ethyl acetoacetate, giving the coumarin (XIII). Acyl derivatives of 1,2,4,5-tetrahydroxybenzene are not easily accessible, and as formyl derivatives appear not to have been obtained before, this preparation is of general interest.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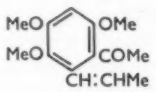
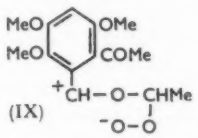

(VIII)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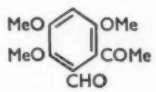
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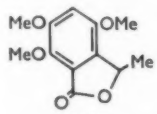
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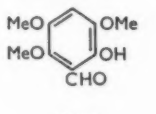
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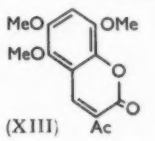
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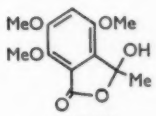
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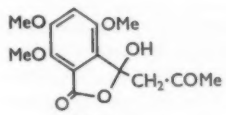
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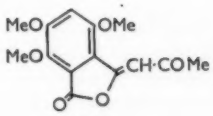
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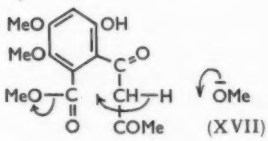
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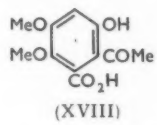
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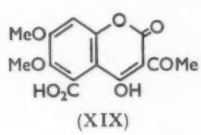
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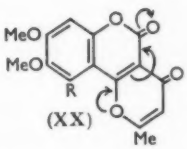
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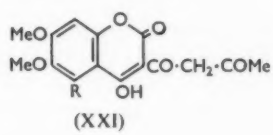
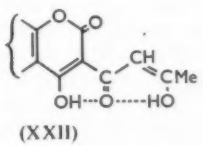

(XXI)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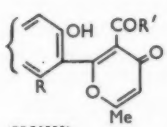
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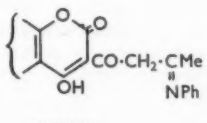
(XXIV)

Permanganate oxidised the aldehyde (X) to the corresponding acid which, like other *o*-acetylbenzoic acids, behaved spectroscopically as the lactol (XIV). In Claisen condensations with methyl acetate and sodium methoxide, this lactol provided a β-diketone which gave a ferric reaction but, on spectroscopic grounds, must also be allocated a lactol structure (XV). Attempts to convert this β-diketone into an acetylindanedione by inducing an internal Claisen reaction with sodium hydride or sodium hydroxide failed, but when the β-diketone was converted into the acetonylidenephthalide (XVI) by thermal dehydration and then treated with sodium methoxide a smooth transformation into the desired product (VI; R = Me) occurred. This was identical with the methyl ether of the degradation product, which is therefore correctly represented as (VI; R = H).

Because Schwerin [6] maintained that the cyclisation of *o*-acetoacetylbenzoic acids to

[6] Schwerin, *Ber.*, 1894, **27**, 104; see Horton and Murdock, *J. Org. Chem.*, 1960, **25**, 938, for further references.

XUM

acetylindanediones is spontaneous, it was suggested that the hydrolytic degradation of citromycetin [2] and fulvic acid [5] derivatives to the indanedione (VI; R = H) occurred by way of the carboxylic acid (III; R = H). This view can no longer be maintained because in this series at least * such acids did not cyclise thus and the efficacy of sodium methoxide alone amongst the bases examined strongly suggests that the essential reaction is the extrusion of methoxide ion from the ester group by the acetoacetyl carbanion as indicated in (XVII). The alkaline hydrolysis of methyl di-*O*-methylcitromycetinone (I; R = Me) has been investigated anew with this point in mind.

Alkali can attack methyl di-*O*-methylcitromycetinone (I; R = Me) at the methoxycarbonyl group and at the pyrone rings, the nature of the products depending on the relative rates. It would be expected that, in so far as the ester group survives, the β-diketone (XVII) would be formed and hence the acetylindanedione which is stable to further attack by bases. If this ester group does not survive, then the β-diketonic carboxylic acid (III) would be produced but would suffer further hydrolysis. In our experience, 2N-sodium hydroxide converts methyl di-*O*-methylcitromycetinone, not only into the acetylindanedione (VI; R = H) in the way described by other workers, but also into the acid (XVIII) not detected previously. The structure of this acid has been confirmed by synthesis (see following paper) and can be regarded as resulting from hydrolysis of acid (III; R = H) as predicted. Moreover, the properties of this acid are in every way identical with those described [3] for the Hetherington–Raistrick " pyrone " except for the analytical data: in spite of this discrepancy we consider that their " pyrone " must have been the acid (XVIII).

The kindness of Dr. W. B. Whalley in providing us with specimens derived from earlier work on citromycetin has allowed us to clarify some other details of the chemistry of this compound. When hydrolysed by 0·5N-sodium hydroxide, methyl di-*O*-methylcitromycetinone (I; R = Me) furnishes the corresponding acid (I; R = H) that is reconverted into the parent ester by diazomethane. The production of this acid had not been recognised in the earlier studies, but it is identical with a hydrolysis product formerly considered to be the coumarin (XIX). In consequence, the observation by Robertson, Whalley, and Yates [2] that the coumarin (XIX) gives very little of the chromone (II) when treated with alkali can now be translated into evidence that the acid (I; R = H) gives very little of the acetylindanedione (VI; R = H): this accords entirely with the present views as to the source of the last-mentioned compound.

Finally, hydrolysis of methyl di-*O*-methylcitromycetinone (XX; R = CO_2Me) by hydrochloric acid had been shown to give the β-diketonic α-pyrone (XXI; R = CO_2Me), whereas hydration on a palladium catalyst had been considered [7] to yield the isomeric γ-pyrone (XXIII; R = CO_2Me, R′ = OH). Similarly, hydrolysis of di-*O*-methylcitromycinone (XX; R = H) had been shown to yield (XXI; R = H), but hydration on a catalyst was considered to give (XXIII; R = H, R′ = OH). Materials obtained by the second method appeared to have properties very similar to those obtained by the first, and in fact specimens prepared by the two methods are spectroscopically identical. The infrared spectrum of compound (XXI; R = H), as a Nujol mull, shows no discrete hydroxylic bands, and no ketonic bands higher than 1600 cm.$^{-1}$, whereas absorption at 1724 cm.$^{-1}$ must be attributed to an α-pyrone ring. Thus there is evidence that the hydrolysis products are of type (XXI) and not of type (XXIII) and that the β-diketones (XXI) exist as hydrogen-bonded enols (XXII). The anilides of type (XXIII; R′ = NHPh) can now be re-formulated as the anils (XXIV), a revision which accounts equally well for their formation from aniline and either the γ-pyrones (XX) or the β-diketones (XXI). This revision is satisfactory on theoretical grounds also, for the electronic interaction indicated in (XX) would reduce the reactivity of the lactonic-carbonyl group to

* The examples given by Schwerin have not been re-examined.

[7] Cavill, Robertson, and Whalley, *J.*, 1950, 1031; Whalley, in " Progress in Organic Chemistry," ed. Cook, Butterworths Scientific Publishers, London, 1958, Vol. IV, p. 72.

bases below that normally found in coumarins, but would much increase that of the γ-pyrone ring.

Experimental

Attempted Methylation of 2-Acetylindane-1,3-dione.—(*a*) When this indanedione (1·0 g.) in boiling acetone (80 ml.) containing potassium carbonate (1·5 g.) and methyl iodide (1 ml.) was treated with further portions (0·3 ml.) of methyl iodide every 3 hr. for 24 hr. some reaction occurred. The product was isolated by evaporating the filtered solution and triturating the residue with saturated aqueous sodium hydrogen carbonate. 2-Acetylindane-1,3-dione (0·6 g.) was recovered by acidification of the orange solution: crystallisation of the colourless residue from benzene–light petroleum (b. p. 60—80°) gave an unidentified substance in the form of plates (0·13 g.), m. p. 190° (Found: C, 75·1; H, 4·5%).

(*b*) The indanedione (0·5 g.) was converted into the sodium salt by the requisite quantity of 2N-sodium hydroxide and when treated with 0·1N-silver nitrate in excess furnished a silver salt. This was washed with water, dried *in vacuo* in the dark, suspended in benzene (10 ml.), and heated with methyl iodide (1 ml.) for 1 hr. The yellow solution was filtered and on evaporation left a brown oil which was dissolved in benzene and washed with aqueous sodium hydrogen carbonate. The neutral material recovered from the benzene crystallised from aqueous methanol, giving yellow plates m. p. 133°. It rapidly decomposed when kept and failed to yield methyl iodide in Zeisel determinations.

2-Acetyl-4,5,7-trimethoxyindane-1,3-dione (VI; R = Me).—(*a*) Obtained by degradation of fulvic acid,[5] 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione (VI; R = H) (0·5 g.) was treated in boiling 5% aqueous sodium hydroxide with methyl sulphate (1 ml.) added gradually during 1 hr. A bright yellow sodium salt slowly separated, and this was collected, suspended in water, and decomposed by being shaken with dilute hydrochloric acid. The remaining solid was still yellow, and when collected and crystallised from methanol afforded the *trimethoxyindanedione* in golden needles (0·3 g.), m. p. 175—176° [Found: C, 60·4; H, 5·3; OMe, 33·3. $C_{11}H_5O_3(OMe)_3$ requires C, 60·4; H, 5·1; OMe, 33·5%]. This compound was soluble in sodium hydrogen carbonate solutions and gave a reddish-brown ferric reaction. It had $\lambda_{max.}$ (in EtOH) 289, 299 mμ (log ε 4·45, 4·45) and (in Nujol) $\nu_{max.}$ 1711, 1643, 1631, and 1605 cm.$^{-1}$: these values compare closely with those of the parent phenol.[5]

This methyl ether (0·15 g.) was oxidised in boiling acetone (15 ml.) by powdered potassium permanganate (0·75 g.) added in small portions during 1·5 hr. After a further ½ hr. at the b. p. the mixture was clarified by addition of water (5 ml.) and passage of a stream of sulphur dioxide. The aqueous solution left after filtration and removal of the acetone was extracted continuously with ether for 3 hr., and the acidic fraction was isolated from the extract by means of sodium hydrogen carbonate. The product, a brown gum, was purified by sublimation at 140°/0·1 mm. The pale green crystalline sublimate (5 mg.) was recrystallised from ethyl acetate–light petroleum (b. p. 60—80°), giving 3,4,6-trimethoxyphthalic anhydride in needles, m. p. and mixed m. p. 210—211°.

(*b*) The acetonylidenephthalide (XVI) (0·05 g.) (see below) was kept in methanol (10 ml.) containing sodium methoxide (0·01 g.) for 12 hr. A yellow sodium salt separated, and this was dissolved in water (5 ml.) and acidified with hydrochloric acid, giving the trimethoxyindanedione which crystallised from methanol in golden needles, m. p. 175—176°, not depressed by admixture with a specimen prepared as in (*a*) above. Samples prepared by methods (*a*) and (*b*) had identical infrared spectra.

2-Acetyl-3,5,6-trimethoxybenzaldehyde (X).—Ozonised oxygen was bubbled through water and then through a solution of 3,4,6-trimethoxy-2-propenylacetophenone [1] (1 g.) in ethyl acetate (20 ml.) at −70°. Separation of a white solid began after about ½ hr., and was complete after 1 hr. This solid crystallised from benzene–light petroleum (b. p. 60—80°), giving the *2-acetylbenzaldehyde* in rosettes of pinkish needles (0·6 g.), m. p. 121—122°, $\lambda_{max.}$ (in EtOH) 223, 272, 339 mμ (log ε 4·14, 3·60, 3·29), $\nu_{max.}$ 1681, 1639, and 1590 cm.$^{-1}$ [Found: C, 60·4; H, 6·0; OMe, 36·2; *C*-Me (Kuhn–Roth), 5·0. $C_9H_5O_2(OMe)_3$ requires C, 60·5; H, 5·9; OMe, 39·1; 1*C*-Me, 6·3%]. This aldehyde rapidly became red when exposed to air. From the mother-liquors a small quantity of the iso-ozonide, m. p. and mixed m. p. 116°, was isolated.

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The *aldoxime*, m. p. 212—214° (decomp.) (Found: C, 56·4; H, 5·8; N, 5·5. $C_{12}H_{15}NO_5$ requires C, 56·9; H, 6·0; N, 5·5%), separated from a solution of the aldehyde (0·2 g.), hydroxylamine hydrochloride (0·5 g.), and sodium acetate (0·2 g.) in alcohol (4 ml.) and water (4 ml.). As it did not crystallise from organic solvents it was purified by repeated precipitation from solutions of its sodium salt by acids. Its unusual properties (reddish-violet ferric reaction and lack of intense absorption in the carbonyl region of the infrared spectrum) are consistent with earlier work on this type of compound.[8]

4,6,7-*Trimethoxy*-3-*methylphthalide* (XI).—When the foregoing aldehyde (0·5 g.) was added in small portions to N-aqueous sodium hydroxide (20 ml.) and shaken it dissolved slowly. The solution was cooled in ice and the product, liberated by dilute hydrochloric acid, was purified from methanol, giving the *phthalide* as needles (0·3 g.), m. p. 140—141°, $\nu_{max.}$ 1764, 1610 cm.$^{-1}$ [Found: C, 60·3; H, 6·0; OMe, 39·3; *C*-Me (Kuhn–Roth), 6·3. $C_9H_5O_2(OMe)_3$ requires C, 60·5; H, 5·9; OMe, 39·1; 1*C*-Me, 6·3%]. This compound, though neutral, dissolved in alkaline media and was recovered by acidification.

2-*Hydroxy*-3,5,6-*trimethoxybenzaldehyde* (XII).—To the foregoing aldehyde (1·5 g.) in methyl acetate (50 ml.) was added a 5% solution (8·5 ml.) of performic acid in formic acid. After 1·5 hr. at 20° and then 0·5 hr. at 90° the cooled mixture was diluted with ether (100 ml.) and extracted with 2N-sodium hydroxide. Acidification of the extract gave crystals which, when recrystallised from light petroleum (b. p. 60—80°), furnished the 2-*hydroxybenzaldehyde* in yellow needles (0·7 g.), m. p. 84° [Found, on specimen dried *in vacuo* at 60°: C, 56·6, 56·7; H, 6·0, 5·7; OMe, 43·6, 43·9. $C_7H_3O_3(OMe)_3$ requires C, 56·6; H, 5·7; 3OMe, 43·9%]. Kuhn–Roth estimations showed that no *C*-methyl groups were present.

A mixture of this salicylaldehyde (0·25 g.) and ethyl acetoacetate (5 ml.) containing a little piperidine slowly solidified. The solid was purified from ethyl acetate; it gave 3-*acetyl*-5,6,8-*trimethoxycoumarin* (XIII) as orange needles (0·12 g.), m. p. 165—166° [Found, on specimen dried *in vacuo* at 110°: C, 60·2; H, 5·2; OMe, 33·3. $C_{11}H_5O_3(OMe)_3$ requires C, 60·4; H, 5·1; OMe, 33·5%], $\nu_{max.}$ 1718 (coumarin C:O) and 1669 cm.$^{-1}$ (αβ-unsaturated ketone).

2-*Acetyl*-3,5,6-*trimethoxybenzoic Acid*.—2-Acetyl-3,5,6-trimethoxybenzaldehyde (2 g.) in acetone (100 ml.) at the b. p. was oxidised by a solution of potassium permanganate (5 g.) and magnesium sulphate (5 g.) in water (100 ml.) added in 3 min. The solution was decolorised by a stream of sulphur dioxide, freed from acetone by distillation, and extracted with chloroform (3 × 50 ml.). From the extracts the desired *acetylbenzoic acid* was isolated by means of aqueous sodium carbonate and crystallised from aqueous alcohol as prisms (0·8 g.), m. p. 180° [Found: C, 56·6; H, 5·7; OMe, 36·6. $C_9H_5O_3(OMe)_3$ requires C, 56·7; H, 5·6; OMe, 36·6%]. Infrared absorption in Nujol mulls ($\nu_{max.}$ 3470, 1748, and 1618 cm.$^{-1}$) suggested that, in the solid state, this acid exists as the lactol (XIV), but the compound was readily soluble in aqueous sodium hydrogen carbonate.

This acid (0·5 g.) was also prepared by oxidising the propenylacetophenone (VIII) (4 g.) in the same way.

2-*Acetoacetyl*-3,5,6-*trimethoxybenzoic Acid*.—Attempts to effect Claisen condensations between the *o*-acetylbenzoic acid (XIV) and methyl acetate by means of sodium methoxide failed when the solvent used was benzene or dioxan. To the acetylbenzoic acid (0·8 g.) in tetrahydrofuran (30 ml.) was added freshly prepared sodium methoxide (2 g.). The mixture was kept at the b. p. for ½ hr. while methyl acetate (2 ml.) diluted by tetrahydrofuran (20 ml.) was run in gradually. After 3 hr. at the same temperature the mixture had deposited a fine yellow powder which was collected, dissolved in iced water, and acidified with hydrochloric acid. The product separated slowly and was crystallised from methanol, giving the o-*acetoacetylbenzoic acid* in plates (0·6 g.), m. p. 167—168° (decomp.) [Found: C, 56·5, 56·8; H, 5·4, 5·7; OMe, 31·6, 31·6; *C*-Me (Kuhn–Roth), 5·2. $C_{11}H_7O_4(OMe)_3$ requires C, 56·8; H, 5·4; OMe, 31·4; 1*C*-Me, 5·1%]. Though this diketone is soluble in aqueous sodium hydrogen carbonate and gives in alcohol a blood-red ferric reaction, the spectroscopic data [$\lambda_{max.}$ (in EtOH) 326 mμ (log ε 3·80); $\nu_{max.}$ 3390 (OH), 1754 (phthalide C:O), 1715 (saturated ketone), and 1613 cm.$^{-1}$] suggest that in the solid state it is present as the lactol (XV).

Heated with 2N-sodium hydroxide (2·5 ml.) on the steam-bath for ½ hr., the β-diketone (0·1 g.) gave an orange solution from which acidification precipitated 2-acetyl-3,5,6-trimethoxybenzoic acid, forming prisms (0·07 g.), m. p. and mixed m. p. 180°, from alcohol.

[8] Griffiths and Ingold, *J.*, 1925, **127**, 1698.

3-*Acetonylidene*-4,6,7-*trimethoxyphthalide* (XVI).—The sublimate obtained when the foregoing β-diketone (0·1 g.) was kept at 200°/0·4 mm. for 15 min. was crystallised from methanol, giving the *acetonylidenephthalide* in long yellow prisms, m. p. 219—220°, $\lambda_{max.}$ (in EtOH) 232, 270, 387 mμ (log ε 4·22, 4·22, 4·18), $\nu_{max.}$ (Nujol) 1783 (3-alkylidenephthalide), 1757sh, 1678 (αβ-unsaturated ketone), and 1603 cm.$^{-1}$ [Found: C, 60·2; H, 5·1; OMe, 32·8, 33·0; *C*-Me (Kuhn–Roth), 4·7. $C_{11}H_5O_3(OMe)_3$ requires C, 60·4; H, 5·1; OMe, 33·4; 1*C*-Me, 5·4%].

The same compound was also produced during an attempt to convert the β-diketone (XV) into an acetylindanedione. This β-diketone (0·1 g.) was heated with sodium hydride (0·05 g.) in boiling pyridine (5 ml.) for 15 min. The cooled solution was treated with a little acetic acid to destroy residual sodium hydride, and then poured into an excess of ice-cold acetic acid. The product was extracted into chloroform, recovered by evaporation, and crystallised from methanol to furnish the acetonylidenephthalide (0·06 g.), m. p. and mixed m. p. 219—220°.

*Alkaline Hydrolysis of Methyl Di-*O*-methylcitromycetinone.*—(a) 2N-*Sodium hydroxide.* The orange solution obtained by boiling methyl di-*O*-methylcitromycetinone (1·0 g.) with 2N-aqueous sodium hydroxide (50 ml.) for ½ hr. was acidified with 2N-sulphuric acid. The yellow precipitate was collected and when crystallised from methanol furnished 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione in needles (0·25 g.), m. p. 157°. Extraction of the filtrate with ether resulted in an orange solution which deposited a white solid after partial concentration: evaporation of the filtrate from the white solid supplied a further quantity (0·07 g.) of the indanedione.

Purified from methanol, the white solid gave 2-*acetyl*-3-*hydroxy*-5,6-*dimethoxybenzoic acid* (XVIII) which formed prisms (0·02 g.), m. p. 181° (decomp.), having a green ferric reaction in alcohol but a purplish-brown ferric reaction in aqueous alcohol [Found: C, 55·3; H, 5·1; OMe, 26·0. $C_9H_6O_4(OMe)_2$ requires C, 55·0; H, 5·0; OMe, 25·8%]. Further details of its properties and a synthesis are recorded in the following paper.

(b) 0·5N-*Sodium hydroxide.* When the orange solution obtained by heating methyl di-*O*-methylcitromycetinone (1·0 g.) with 0·5N-aqueous sodium hydroxide (50 ml.) on the steam-bath for 1 hr. was acidified, ether-extraction removed from it a little 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione (0·05 g.). When the extracted solution was kept, an ether-insoluble solid gradually separated and was purified from a large volume of methanol. Obtained thus, *di*-O-*methylcitromycetinone* (I; R = H) formed long needles (0·2 g.), m. p. 314° (decomp.) (Found, on specimen dried at 140° *in vacuo* for 8 hr.: C, 57·4; H, 3·9. $C_{16}H_{12}O_8$ requires C, 57·8; H, 3·6%). This acid had $\nu_{max.}$ (in Nujol) 3610, 3472, 3367 (partially bonded OH of CO_2H), 1754 (α-pyrone C:O), 1695 (carboxyl C:O), 1661 (γ-pyrone C:O), 1623, and 1597 cm., and was identified by mixed fusion and spectroscopically with a specimen of the substance prepared by Robertson, Whalley, and Yates [2] and regarded by them as the 3-acetylcoumarin (XIX). Diazomethane rapidly reconverted this acid into methyl di-*O*-methylcitromycetinone, m. p. and mixed m. p. 240°, further identified spectroscopically.

We thank Mr. C. Tomlinson, Mr. D. Newman, and their colleagues for the microanalyses and Mr. J. Barkley for the infrared determinations. We also thank Messrs. T. J. Hughes for grants made to D. R. R. and G. W.

THE UNIVERSITY OF LIVERPOOL. [*Received, August 10th*, 1960.]

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171. *Derivatives of Hydroxyquinol. Part III.*[1] *The Structure of Fulvic Acid: Syntheses and Reactions of Degradation Products of Fulvic Acid and of Citromycetin.*

By F. M. Dean and D. R. Randell.

Methyl 6,7-dimethoxy-2-methylchromone-5-carboxylate has been synthesised and shown to reproduce the spectroscopic properties of the appropriate derivatives of fulvic acid and to be converted by alkali in the predicted way into 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione. These facts taken with data from nuclear magnetic spectra confirm the structure for fulvic acid proposed earlier.

2-Acetyl-3-hydroxy-5,6-dimethoxybenzoic acid and 4-hydroxy-6,7-dimethoxycoumarin-5-carboxylic acid have been synthesised and identified with degradation products of citromycetin. 3-Acetyl-4-hydroxy-6,7-dimethoxycoumarin-5-carboxylic acid has also been synthesised and shown to differ from the product which had been obtained by degradation of citromycetin and allocated this structure.

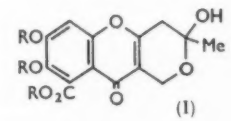
Although studies of fulvic acid were believed to indicate structure (I; R = H) for this compound, none of the simpler degradation products appeared to retain the chromone ring fundamental to this structure.[2] Thus alkaline hydrolysis of methyl anhydrodi-*O*-methylfulvate (II) was considered to involve opening of both heterocyclic rings, giving an intermediate (III) which then suffered both β-diketonic fission and retroaldol condensation leading to an *o*-acetoacetylbenzoic acid (IV; R = H) or its ester (IV; R = Me). A similar sequence had been invoked[3] to account for the alkaline degradation of methyl di-*O*-methylcitromycetinone (V; R = Me) which had led to a product regarded as the chromone-5-carboxylic acid (VI; R = H). This chromone was thought to be formed by cyclisation of the phenolic β-diketonic system in (IV; R = H or Me). In Part II (preceding paper), however, it was proved that this degradation product is not a chromone but the acetylindanedione (VII) formed by the alternative cyclisation of (IV; R = Me) in which the β-diketonic side-chain becomes linked, not to the hydroxyl, but to the ester grouping. The elusive chromone (VI; R = Me) has now been synthesised and converted into the indanedione (VII) in the conditions used for the degradation of methyl anhydrodi-*O*-methylfulvate (II) and methyl di-*O*-methylcitromycetinone (V; R = Me). Moreover, the close similarities in both the ultraviolet and the infrared spectra obtained from the chromone ester (VI; R = Me) and from the appropriate derivatives of fulvic acid (I; R = H) confirm that this compound is indeed a chromone; and this fact, taken with evidence from the nuclear magnetic resonance spectrum of methyl anhydrodi-*O*-methylfulvate (II), leaves no doubt that fulvic acid does have structure (I; R = H).

Unlike the corresponding trimethyl ether,[1,4] the benzyl ether (VIII) affords neither a stable iso-ozonide nor the desired aldehyde when treated with ozone: apparently the benzyl group is attacked at the same time as the propenyl substituent. Permanganate oxidation of the benzyl ether (VIII) led in moderate yield to an *o*-acetylbenzoic acid which behaved as the lactol (IX; R = CH_2Ph). Hydrogenolysis of this lactol was unsatisfactory when a palladium catalyst was used, but with Raney nickel the phenolic acid (X) was readily obtained and its properties suggested that chelation prevents its forming a lactol comparable to (IX). As mentioned in Part II, this acid is identical with one of the products obtained by alkaline degradation of methyl di-*O*-methylcitromycetinone (V; R = Me) and is presumably the substance which Hetherington and Raistrick believed to be a pyrone.

[1] Part II, preceding paper.
[2] Dean, Eade, Moubasher, and Robertson, *J.*, 1957, 3497.
[3] Robertson, Whalley, and Yates, *J.*, 1951, 2013.
[4] Dean, Randell, and Winfield, *J.*, 1959, 1071.

Although the phenolic acid (X) failed to undergo Claisen condensations with methyl acetate in a wide variety of conditions, the derived acetate [actually the lactol (IX; R = Ac)] rearranged in Baker–Venkataraman conditions. The expected β-diketone (IV; R = H) could not be obtained, however, since when liberated from its sodium salt it at once gave the chromone-5-carboxylic acid (VI; R = H): cyclisation to a chromone was expected at this point because it had been shown in Part II that indanedione formation would be restricted to the ester (IV; R = Me). In support of this view the chromone-5-carboxylate (VI; R = Me), obtained from the acid by means of diazomethane, rapidly changed into the 2-acetylindane-1,3-dione (VII) when treated with base, and the compound so made was identical with specimens obtained from degradation of fulvic acid or of citromycetin.

Of the transformation products of fulvic acid, two, methyl di-*O*-methylfulvate (I; R = Me) and methyl deoxydi-*O*-methylfulvate (XI), have been allocated structures [2] which should show much the same spectroscopic behaviour as the chromone-5-carboxylate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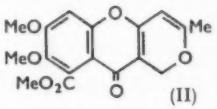
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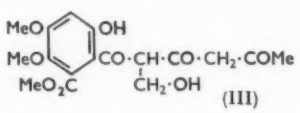
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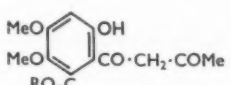
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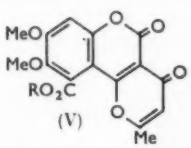
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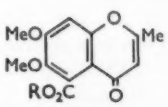
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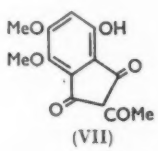
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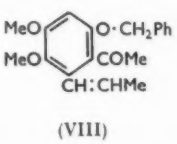
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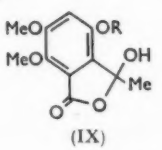
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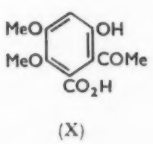
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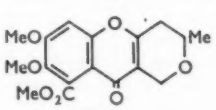
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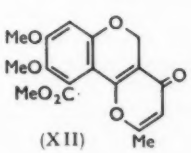
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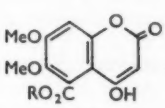
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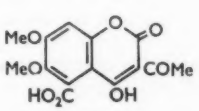
(XIV)

(VI; R = Me). With one exception (a band at 1623 cm.$^{-1}$ in the infrared spectrum of methyl deoxydi-*O*-methylfulvate for which we cannot account) the spectroscopic properties of all three compounds are so closely similar (Tables 1 and 2) that the formulation of fulvic as a chromone can hardly be doubted. Methyl anhydrodi-*O*-methylfulvate (II) and methyl di-*O*-methylcitromycetin (XII) are isomeric and have similar structural units. Their nuclear magnetic resonance spectra should therefore be comparable, Table 3 showing that this is so. That a band allocated to the methylene group in :C·CH_2·O· should appear was particularly welcome, since this methylene group had defied chemical identification during degradative studies on fulvic acid.[2] Consequently, we are now confirmed in our belief that fulvic acid has structure (I; R = H).

A very minor hydrolysis product from methyl di-*O*-methylcitromycetinone (V; R = Me) has been formulated [3] as a 4-hydroxycoumarin-5-carboxylic acid (XIII; R = H), and the corresponding ester (XIII; R = Me) has been obtained [3] by permanganate oxidation of methyl anhydrodi-*O*-methylfulvate (II). While the phenolic acid (X) did not condense

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directly with ethyl carbonate, its ethoxycarbonyl derivative cyclised to the 4-hydroxycoumarin (XIII; R = H) when treated with sodium methoxide. The synthetic product has the properties described for the citromycetin degradation product, but a direct identification could not be effected since the necessary specimen was not available and we failed to isolate the appropriate material by following the prescribed degradative route. Moreover, we failed to hydrolyse the coumarin-5-carboxylate (XIII; R = Me) to the corresponding acid using conditions designed to avoid collapse of the pyrone ring, and also failed to induce satisfactory esterification by treating the acid with diazomethane. Therefore we have been unable to identify either of the degradation products unequivocally,

TABLE 1. *Infrared frequencies* * (*cm.*$^{-1}$) *in the* 6μ *region.*

	Ester	Chromone carbonyl	Other absorption	
Me 6,7-dimethoxy-2-methylchromone-5-carboxylate ...	1735	1650	—	1600
Me di-*O*-methylfulvate	1742	1647	—	1592
Me deoxydi-*O*-methylfulvate	1740	1647	1623	1603

* In Nujol mulls. All strong bands.

TABLE 2. *Ultraviolet characteristics* (*in alcohol;* log ε *in parentheses*).

Me 6,7-dimethoxy-2-methylchromone-5-carboxylate	232 (4·34), 277 (4·03), 306 mμ (4·01)
Me di-*O*-methylfulvate	230 (4·41), 282 (4·08), 300 mμ (3·99)
Me deoxydi-*O*-methylfulvate	230 (4·40), 282 (4·08), 303 mμ (4·00)

TABLE 3. *Nuclear magnetic resonance spectra*[a] *of methyl di-*O*-methylcitromycetin* (XII) *and of methyl anhydrodi-*O*-methylfulvate* (II).

Band	Compound (XII)	Compound (II)	Relative intensity	Assignment
0–1	31·3[c]	19·3[c]	1	ArH
0–2	49·2	80·0	1	C:CH[b]
0–3	87·5	85·5	2	O·CH$_2$·C:[c]
0–4	133	136	3	OCH$_3$
0–5	135·5	139·5	3	OCH$_3$
0–6	138·5	143	3	OCH$_3$
[0–7]	180[d]	213[d]	$\ll$1	?
0–8	199	219	3	:C·CH$_3$[b]

[a] H^1 Resonance at 40·00 Mc./sec. in chloroform as solvent and with chloroform as reference compound. Shifts in c./sec. [b] In ·CH:C·CH$_3$ but not in C:CH·CH$_3$. [c] In O·CH$_2$·C: but not in O·CH$_2$·CH:. [d] The source of these weak signals is not known.

though the spectroscopic and other data leave little doubt that these products have been correctly formulated.

Finally, the 4-hydroxycoumarin (XIII; R = H) was converted into its 3-acetyl derivative (XIV) by the boron fluoride–acetic anhydride technique.[5] The product was widely different from a substance which had been obtained[3] by hydrolysis of methyl di-*O*-methylcitromycetinone (V; R = Me) and shown to be di-*O*-methylcitromycetinone (V; R = H) in Part II. Like the parent compound[5] (XIV less the carboxyl group) this 3-acetyl-4-hydroxycoumarin could not be further acylated, so we could not synthesise di-*O*-methylcitromycetinone (V; R = H) from it.

EXPERIMENTAL

2-Acetyl-3-benzyloxy-5,6-dimethoxybenzoic Acid.—A hot solution of potassium permanganate (7·5 g.) and magnesium sulphate (7·5 g.) in water (150 ml.) was added in 5 min. to 6-benzyloxy-3,4-dimethoxy-2-propenylacetophenone[4] (3·0 g.) in boiling acetone (150 ml.), and the mixture was filtered at once to remove manganese dioxide. The filtrate was decolorised by means of sulphur dioxide and freed from acetone by evaporation. The product was isolated by extraction from the aqueous residue into chloroform, and thence into 2N-sodium carbonate. Precipitated by acidification, the *benzyloxybenzoic acid* formed plates (0·37 g.), m. p. 150—151°,

[5] Badcock, Dean, Robertson, and Whalley, *J.*, 1950, 903.

from aqueous methanol [Found: C, 65·1; H, 5·5; OMe, 19·2. $C_{16}H_{12}O_4(OMe)_2$ requires C, 65·4; H, 5·5; OMe, 18·8%]. In the solid state in Nujol mulls this acid had $\nu_{max.}$ 3472 (OH), 1748 (phthalide C:O), and 1608 cm.$^{-1}$, and therefore exists as the lactol (IX; R = CH_2Ph). When the oxidation was effected in more vigorous conditions the yield of the benzyloxybenzoic acid decreased and benzoic acid was also isolated.

2-Acetyl-3-hydroxy-5,6-dimethoxybenzoic Acid (X).—The foregoing benzyloxybenzoic acid (2·0 g.) in 2N-sodium hydroxide (60 ml.) was shaken with Raney nickel (~1 g.) and hydrogen. Absorption ceased after about 4 hr., and acidification of the filtered solution then gave 2-acetyl-3-hydroxy-5,6-dimethoxybenzoic acid which separated from aqueous alcohol in prisms (1·2 g.), m. p. 181° (decomp.) [Found: C, 55·2; H, 5·1; OMe, 25·5. Calc. for $C_9H_6O_4(OMe)_2$: C, 55·0; H, 5·0; OMe, 25·8%]. This acid dissolved readily in sodium hydrogen carbonate solution: the green colour it imparted to alcoholic ferric chloride became purplish-brown on the addition of water. In mulls it strongly absorbed infrared radiation at 3356, 3215 (bonded OH), 1718 (CO_2H), 1709sh, and 1613 cm.$^{-1}$ (chelated acetophenone C:O) and therefore showed no tendency to form a lactol. It was identified by the mixed-fusion and infrared techniques with one of the alkali-degradation products of methyl di-*O*-methylcitromycetinone (see Part II).

The *acetate* was prepared by shaking a solution of the acid (0·6 g.) in 2N-aqueous sodium hydroxide (15 ml.) with acetic anhydride (2 ml.) added dropwise during 15 min. at 0°, and it crystallised from benzene–light petroleum (b. p. 60—80°) in rectangular prisms (0·5 g.), m. p. 161° [Found: C, 55·3; H, 5·2; OMe, 22·1. $C_{11}H_8O_5(OMe)_2$ requires C, 55·3; H, 5·0; OMe, 22·0%]. This acetate appeared to be the lactol (IX; R = Ac) since it had $\nu_{max.}$ 3436, 3067, 1754, and 1600 cm.$^{-1}$ but no ketonic absorption.

6,7-Dimethoxy-2-methylchromone-5-carboxylic Acid (VI; R = H).—3-Acetoxy-2-acetyl-5,6-dimethoxybenzoic acid (0·70 g.) was treated with powdered sodium (0·4 g.) in tetrahydrofuran (40 ml.) at 90°. After 3 hr. the mixture was cooled and, after residual sodium had been destroyed by a little alcohol, diluted with ether (100 ml.). The orange sodium salts were then extracted into water. The extract was saturated with ammonium sulphate and acidified with hydrochloric acid. The yellow solid produced crystallised from 95% alcohol, giving the *chromone acid* in prisms (0·2 g.), m. p. 276° (decomp.) (Found, on specimen dried *in vacuo* at 140°: C, 58·9; H, 4·7. $C_{13}H_{12}O_6$ requires C, 59·1; H, 4·6%). This compound had $\nu_{max.}$ 3145 (CO_2H), 1733 (CO_2H), 1639 (chromone C:O), and 1595 cm.$^{-1}$: it gave no ferric reaction.

Similar results were obtained when the reaction was carried out in pyridine with sodium hydride or in tetrahydrofuran with sodium methoxide, but the yields were less good.

Diazomethane converted the acid in ether–methanol into the *methyl ester* which separated from benzene–light petroleum (b. p. 60—80°) in rectangular prisms, m. p. 135° (Found, on specimen dried *in vacuo* at 110°: C, 60·3; H, 5·1. $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·1%).

2-Acetyl-7-hydroxy-4,5-dimethoxyindan-1,3-dione (VII).—When methyl 6,7-dimethoxy-2-methylchromone-5-carboxylate (0·02 g.) and 2N-aqueous sodium hydroxide (0·2 ml.) were heated together in methanol (2 ml.) on a steam-bath for 15 min., an orange solution was formed and then a yellow solid separated. This solid was collected, washed with methanol, and treated with dilute hydrochloric acid to give a buff-coloured product which, when purified from methanol, afforded 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione in pale yellow needles, m. p. 157° (Found: C, 58·9; H, 4·7. Calc. for $C_{13}H_{12}O_6$: C, 59·1; H, 4·6%). This compound was identical with specimens of " Compound B " prepared from methyl di-*O*-methylcitromycetinone or from methyl di-*O*-methylanhydrofulvate.

4-Hydroxy-6,7-dimethoxycoumarin-5-carboxylic Acid (XIII; R = H).—2-Acetyl-3-hydroxy-5,6-dimethoxybenzoic acid (0·6 g.) in 0·5N-aqueous sodium hydroxide (10 ml.) was allowed to react with methyl chloroformate (0·25 ml.) at 0° for 15 min. The precipitate formed when the resulting solution was acidified with dilute hydrochloric acid was collected, washed with water, and crystallised from aqueous methanol, giving *2-acetyl-3-methoxycarbonyloxy-5,6-dimethoxybenzoic acid* as hexagonal plates (0·5 g.), m. p. 168° (Found, on specimen dried *in vacuo* at 100°: C, 52·5; H, 4·8. $C_{13}H_{14}O_8$ requires C, 52·4; H, 4·7%). This compound appeared to exist as the lactol (IX; R = CO_2Me) since it had $\nu_{max.}$ (in Nujol) 3401 (OH), 1770 (ArO·CO_2Me), 1745 (phthalide C:O) and 1605 cm.$^{-1}$. It did not give a ferric reaction but was slowly soluble in aqueous sodium hydrogen carbonate.

After this 3-methoxycarbonyloxybenzoic acid (0·60 g.) had been subjected to the action of powdered sodium (0·2 g.) in boiling tetrahydrofuran (20 ml.) for 5 hr., the sodium salts formed were collected, dissolved in water, and decomposed by dilute hydrochloric acid. The solid

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produced was fractionally crystallised from aqueous methanol. The less soluble fractions consisted of 2-acetyl-3-hydroxy-5,6-dimethoxybenzoic acid (0·05 g.), the more soluble of the desired product, which, when further purified from aqueous methanol, afforded *4-hydroxy-6,7-dimethoxycoumarin-5-carboxylic acid* as rhombs (0·11 g.), m. p. 256° (decomp.), soluble in aqueous sodium hydrogen carbonate, giving an amber ferric reaction, and having $\lambda_{max.}$ (in EtOH) 286, 316 mμ (log ε 4·37, 4·56) and $\nu_{max.}$ (in Nujol) 3534sh, 3436, 2770—2570 (ill-defined), 1733, 1704, 1669, and 1600 cm.$^{-1}$ (Found, on specimen dried *in vacuo* at 140°: C, 53·8; H, 4·0. $C_{12}H_{10}O_7$ requires C, 54·1; H, 3·8%).

3-Acetyl-4-hydroxy-6,7-dimethoxycoumarin-5-carboxylic Acid (XIV).—The foregoing 4-hydroxycoumarin (33 mg.), acetic anhydride (0·1 ml.), and a saturated solution (0·2 ml.) of boron fluoride in acetic acid were heated together at 90° for 15 min. A yellow boron complex (25 mg.) separated. This was crushed under ether (3 ml.), collected, and dissolved in 5% aqueous sodium acetate (1 ml.), giving a colourless solution which was then acidified. The precipitate separated from methanol, giving *3-acetyl-4-hydroxy-6,7-dimethoxycoumarin-7-carboxylic acid* in hexagonal prisms (17 mg.), m. p. 256° (decomp.), soluble in aqueous sodium hydrogen carbonate, giving an orange-red ferric reaction, and having $\lambda_{max.}$ (in EtOH) 343 mμ (log ε 4·25) and $\nu_{max.}$ (in Nujol) 1736sh, 1724 (coumarin C:O), 1701sh, and 1603 cm.$^{-1}$ (Found, on specimen dried *in vacuo* at 140°: C, 54·3; H, 4·1. $C_{14}H_{12}O_8$ requires C, 54·6; H, 3·9%).

We thank Mr. C. Tomlinson, Mr. D. Newman, and their associates for the microanalyses, and Mr. J. Barkley for the infrared determinations. We are grateful to Dr. L. Sutcliffe and Mr. J. Feeney for supplying and interpreting the nuclear magnetic resonance spectra.

THE UNIVERSITY OF LIVERPOOL. [*Received, August 10th*, 1960.]

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172. *Aromatic Polyfluoro-compounds. Part VII.*[1] *The Reaction of Pentafluoronitrobenzene with Ammonia.*

By G. M. BROOKE, J. BURDON, and J. C. TATLOW.

Treatment of pentafluoronitrobenzene, prepared in 85% yield by the oxidation of pentafluoroaniline with peroxytrifluoroacetic acid, with ammonia gives, depending on the conditions, 2,3,4,5-tetrafluoro-6-nitro- (II) and 2,3,5,6-tetrafluoro-4-nitro-aniline (IV), and 4,5,6-trifluoro-2-nitro- (III) and 2,4,5-trifluoro-6-nitro-1,3-phenylenediamine (V), and 2,4-difluoro-6-nitrobenzene-1,3,5-triamine (VI). The ratio of *ortho-* to *para*-replacement (relative to NO_2) in the initial reaction is about 7 : 3.

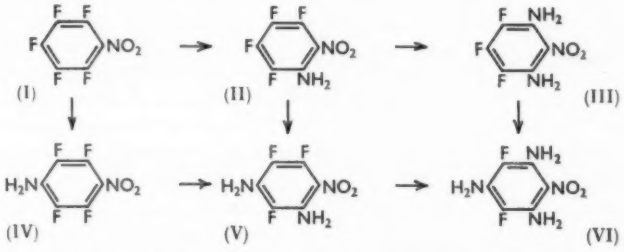
IN a previous paper[2] we described the reaction of penta- and hexa-fluorobenzene with various nitrogen-containing bases to give the corresponding polyfluoro-aromatic bases by the nucleophilic release of fluoride ion. We have now found that pentafluoronitrobenzene (I) reacts with ammonia in a similar manner, but under very much milder conditions, to give a series of fluoronitroanilines as outlined in the annexed scheme.

Pentafluoronitrobenzene was prepared in 85% yield by the oxidation of pentafluoroaniline with peroxytrifluoroacetic acid: Emmons[3] has used this reagent to oxidise a number of aromatic primary amines to nitro-compounds.

Treatment of pentafluoronitrobenzene (I) in ether with ammonia at room temperature gave, in good yield, a product which when dissolved in benzene was separated into three coloured bands on passage through a chromatographic column packed with alumina. The second of these bands was a mixture of two components (III and IV), which had to be separated by crystal-picking. The first [compound (II)] and the last [compound (V)] band were pure.

[1] Part VI, Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754.
[2] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.
[3] Emmons, *J. Amer. Chem. Soc.*, 1954, **76**, 3470.

Two of these four components (II and IV) together made up about 95% of the product: both were tetrafluoronitroanilines. On hydrogenation over Raney nickel they gave the corresponding tetrafluorophenylenediamines, which were both different from the known [2,4] 2,4,5,6-tetrafluoro-1,3-phenylenediamine. The original nitroanilines must therefore have had the amino- and the nitro-group in *ortho*- and *para*-relation. They were distinguished



by condensation of one of the diamines with trifluoroacetic anhydride, with cyanogen bromide, and with carbonyl chloride to give, respectively, 4,5,6,7-tetrafluoro-2-trifluoromethylbenzimidazole, 2-amino-4,5,6,7-tetrafluorobenzimidazole and 4,5,6,7-tetrafluoro-2,3-dihydro-2-benzimidazolone. The last compound was identical with material derived [5] from 3,4,5,6-tetrafluorophthalic acid *via* a Curtius degradation reaction. The original diamine and the nitroaniline (II) must, therefore, have been the *ortho*-isomers and the other pair the *para*-isomers, although an attempted oxidation of the tetrafluoro-*p*-diamine to the known [6,7] tetrafluoro-*p*-benzoquinone was unsuccessful.

These structures were confirmed by nuclear magnetic resonance spectroscopy. The tetrafluoro-*p*-nitroaniline (IV) showed only two magnetically different types of fluorine atom, while the isomer (II) showed four. The tetrafluoro-1,4-phenylenediamine showed only one type of fluorine atom and the 1,2-isomer showed two (the 1,3-isomer shows [2,8] three).

Further reaction of the *p*-nitroaniline (IV) with ammonia in ether was only slow, so it was carried out in aqueous ethanol at room temperature. This gave a product which was separated into three components by chromatography of its benzene solution on alumina. The fastest-running was the unchanged nitroaniline (IV); the second, a yellow solid, was identical with one of the minor components from the original reaction. Since this was a trifluoronitrophenylenediamine and since it was also obtained by the further ammoniation of the *o*-nitroaniline (II) (see below), it could only have been the 1,3-diamine (V). Nuclear magnetic resonance was in agreement with this; three magnetically different fluorine atoms were found. Further confirmation was supplied by the nuclear magnetic resonance spectrum of the triamine (VII) obtained from this compound (V) by hydrogenation: this showed three different types of fluorine atom, which can only occur in a 1,2,4-triamine. The last component obtained from the reaction of the nitroaniline (IV) with ammonia was a deep red solid and was identical with the triamine (VI) prepared by drastic treatment of the diaminonitro-compounds (III and V) with ammonia (see below).

Reaction of the *o*-nitroaniline (II) with ammonia in ether was also slow. Reaction in ethanol gave four components which were separated by chromatography on alumina. The fastest-moving was the ethoxy-amine (VIII). This structure was indicated by analysis, by synthesis from the *o*-nitroaniline (II) and sodium ethoxide, and by analogy with the structure of the major ammoniation product (V). Presumably, in ethanol–ammonia mixtures two nucleophilic species exist: ethoxide ion and ammonia, the latter

[4] Robson, Roylance, Stephens, and Tatlow, unpublished work.
[5] Chaudhry, Gething, Patrick, Stephens, and Tatlow, unpublished work.
[6] Nield and Tatlow, *Tetrahedron*, 1960, **8**, 38.
[7] Wallenfels and Draper, *Chem. Ber.*, 1957, **90**, 2819.
[8] Homer and Thomas, unpublished work.

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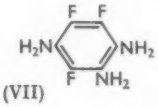
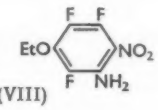
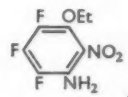
being more important so that attack by ethoxide ion is possible but occurs to a smaller extent. The second component, forming red crystals, was identical with one of the minor components obtained from the reaction of pentafluoronitrobenzene with ammonia in ether. It appeared to be the diamine (III) from its analysis and nuclear magnetic resonance (only two groups of fluorine resonances were shown, one twice as strong as the other); also, since


(VII)


(VIII)


(IX)

the general pattern of replacement of pentafluoronitrobenzene seems to be *ortho* and *para* to the nitro-group, it is reasonable to suppose that ammoniation of the *o*-nitroaniline (II) would give both the 1,3-diamines (III and V). The third component from the reaction of the *o*-nitroaniline (II) with ammonia was the nitro-diamine (V), that was also obtained from the *p*-nitroaniline (IV). The last component, a minor one, was the nitro-triamine (VI). A minute amount of another, red, band was found between bands two and three: it could well have been the ethoxy-analogue (IX) of the minor ammoniation product (III), but it has not been investigated in detail.

Treatment of either nitro-diamine (III or V) with ammonia in aqueous ethanol at 135° for several hours gave good yields of the deep red triamine (VI) obtained previously. If the structures of the nitro-diamines (III and V) are correct then this compound must be 2,4-difluoro-6-nitrobenzene-1,3,5-triamine (VI). Nuclear magnetic resonance confirmed this structure: only one fluorine resonance was observed. This compound was best obtained by the treatment of the *p*-nitroaniline (IV) with ammonia under similar conditions.

We have found no evidence in these reactions for displacement of the nitro-group although this could have taken place to a small extent since our isolation procedure depends on the colour of the products and any product from which the nitro-group had been displaced should be colourless.

The ratio of *ortho*- to *para*-replacement in the initial reaction of pentafluoronitrobenzene with ammonia is about 7 : 3. This is the first example we have found of a predominately *ortho*-reaction in the polyfluoro-aromatic field. In most other cases studied so far, such as reactions with pentafluorobenzene,[1,2] pentafluoroanisole,[6,9] and pentafluorotoluene,[10] replacement occurs mainly *para* to the non-fluorine position. In the reaction of pentafluoroaniline with ammonia, however, it is in the *meta*-position.[2] Considering the example of pentafluorobenzene, the directing of replacement almost exclusively into the *para*-position with respect to the hydrogen appears to be due to the five fluorine atoms. Electrophilic substitution in fluorobenzene takes place mainly in the *para*-position. In nucleophilic substitution, therefore, this position should be least reactive. For pentafluorobenzene then, the combined effect of the five fluorine atoms should leave the fluorine *para* to the hydrogen most susceptible to nucleophilic replacement, in accord with the experimental results. Substituents in place of hydrogen can be considered as having a modifying influence on this directing effect of the five fluorine atoms. Groups only weakly electron-attracting or -repelling would be expected only to influence the relative rate of replacement of the fluorine atom *para* to them. However, strongly electron-repelling groups should increase, by a conjugative mechanism, the electron density at the *para*- (and *ortho*-) more than at the *meta*-position; the amount of *meta*-replacement, as compared with pentafluorobenzene, should therefore increase while the overall rate of reaction decreases. A case of this occurs [2] in the reaction of pentafluoroaniline with ammonia,

[9] Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.
[10] Coe, Barbour, Buxton, Stephens, and Tatlow, Part VIII, following paper.

from which only the *m*-diamine has been isolated. From other studies [11] on nucleophilic aromatic substitution it appears that the amino-group is the most deactivating group known. Since the methoxyl-group is also [11] powerfully deactivating and since the major substitution product of pentafluoroanisole [6,9] is the *para*-isomer, the influence of the five fluorine atoms must be considerable.

Strongly electron-attracting substituents, on the other hand, should decrease the electron densities at the *ortho*- and *para*-positions and increase the reaction rate. This is the case with the reaction of pentafluoronitrobenzene described in this paper. Although the *ortho* : *para* ratio in this reaction is not far from statistical, the nitro-group must nevertheless have a strong *ortho*-directing influence, since pentafluorobenzene, with its electronically neutral hydrogen substituent, is substituted almost entirely [1,2] in the *para*-position. The nitro-group has previously [11] been observed to be more activating, in most cases, from the *ortho*-position than from the *para* in nucleophilic reactions. This greater amount of *ortho*- than *para*-replacement might arise because the *ortho*- is nearer than the *para*- to the nitro-group; this proximity must also be sufficient, in the pentafluoronitrobenzene case, to overcome the *para*-directing effect of the five fluorine atoms.

That the nitroanilines (II and IV) react with ammonia under very much milder conditions than pentafluorobenzene does [2] suggests that the nitro-group activates much more powerfully than the amino-group deactivates.

A surprising feature of these ammoniations is that, although pentafluoronitrobenzene undergoes predominantly *ortho*-reaction, the *o*-nitroaniline (II) reacts predominantly at the position *para* to the nitro-group.

Experimental

An entry " i.r." denotes that the compound was identified by infrared spectroscopy.

Pentafluoronitrobenzene [with R D. Richardson].—A mixture of methylene chloride (100 ml.), trifluoroacetic anhydride (25 ml.), and *ca.* 90% hydrogen peroxide (10 ml.) was refluxed and stirred for 15 min. Pentafluoroaniline [2] (10·3 g.) in methylene chloride (50 ml.) was then added slowly at reflux temperature with stirring. The reaction mixture became dark green in a few minutes. Further hydrogen peroxide (5 ml.) was added after 1 hr., followed 2½ hr. later by more hydrogen peroxide (5 ml.) and trifluoroacetic anhydride (5 ml.). After being refluxed and stirred for 18 hr. in all, the mixture was cooled and water (100 ml.) was added slowly. The methylene chloride layer was separated, washed with water (100 ml.), and dried ($MgSO_4$). Removal of the solvent by fractional distillation through a 6″ column packed with glass helices, followed by simple distillation gave lachrymatory, golden-yellow *pentafluoronitrobenzene* (10·2 g.), b. p. 158—161° (mainly 158·5—160·0°) (Found: C, 33·9. $C_6F_5NO_2$ requires C, 33·8%), $\lambda_{max.}$ 224 mμ (ε 6200 in EtOH).

Removal of the methylene chloride by simple distillation caused losses of pentafluoronitrobenzene by co-distillation.

Reaction of Pentafluoronitrobenzene with Ammonia in Ether.—Ammonia was bubbled slowly through a solution of pentafluoronitrobenzene (3·01 g.) in ether (200 ml.) for 6 hr. After being kept at room temperature for 18 hr., the red solution was filtered to remove ammonium fluoride, and the filtrate was evaporated to dryness *in vacuo* to leave the crude product (2·91 g.). This was chromatographed on a column (20 × 1¼″) packed with alumina (commercial chromatography-grade alumina was used; the properties of this varied from batch to batch; sometimes the untreated material gave a satisfactory separation, but with many batches it was necessary to pre-treat the alumina with water). Benzene was used as eluant. Three bands developed. The first two were washed off with benzene and the third was removed mechanically from the column, and the component washed from the alumina with ethanol. Solvents were removed *in vacuo*, to avoid co-distillation.

Band 1. A bright yellow solid (1·73 g.), m. p. 35—41°, when recrystallised from benzene–light petroleum (b. p. 60—80°), gave *2,3,4,5-tetrafluoro-6-nitroaniline* (II) (0·63 g.), m. p. 42·5—43·5° (Found: C, 34·4; H, 1·2; F, 36·0. $C_6H_2F_4N_2O_2$ requires C, 34·3; H, 1·0; F, 36·2%). The nuclear magnetic resonance spectrum of a 3M-solution in acetone showed four bands, of equal intensity, centred at 70·3, 73·5, 83·3, and 99·0.

[11] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

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It gave a *trifluoroacetyl derivative*, m. p. 80—80·5° [from light petroleum (b. p. 80—100°)] (Found: C, 31·2; H, 0·6. $C_8HF_7N_2O_3$ requires C, 31·4; H, 0·3%).

Band 2. An orange solid (0·78 g.), m. p. 100—106·5°, recrystallised as above, gave a yellow and a minor red component. The major component was purified by further recrystallisation and was 2,3,5,6-*tetrafluoro*-4-*nitroaniline* (IV) (0·54 g.), m. p. 106·5—108° (Found: C, 34·4; H, 1·4; F, 35·8%). Nuclear magnetic resonance of a 2·5M-solution in acetone showed two identical bands of equal intensity centred at 72·3 and 85·8.

This compound gave a *trifluoroacetyl derivative*, m. p. 107·5—108° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 31·4; H, 0·7%).

Less than 10 mg. of the minor component were formed in a single experiment. It was isolated by combination of the mother-liquors from several experiments, evaporation, recrystallisation [from benzene–light petroleum (b. p. 60—80°)], and hand-picking of the crystals. Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave 4,5,6-*trifluoro*-2-*nitro*-1,3-*phenylenediamine* (III), m. p. 162—163·5° (Found: C, 34·5; H, 2·3; F, 27·1. $C_6H_4F_3N_3O_2$ requires C, 34·8; H, 1·9; F, 27·5%). The nuclear magnetic resonance spectrum of a 3M-solution in acetone showed two bands of intensity 1 : 2 at 74·8, and 98·8, respectively.

Band 3. A bright yellow solid (0·07 g.), m. p. 139·5—145°, recrystallised from benzene to give 2,4,5-*trifluoro*-6-*nitro*-1,3-*phenylenediamine* (V) (0·04 g.), m. p. 146·5—148° (Found: C, 34·4; H, 1·9; F, 27·2%). A M-solution in acetone had bands of equal intensity at 72·7, 85·3, and 95·8 in its nuclear magnetic resonance spectrum.

Treatment of the Monoamines (II and IV) *with Ammonia in Ethanol.*—(a) 2,3,4,5-*Tetrafluoro*-6-*nitroaniline* (II). Ammonia was bubbled through a solution of the compound (0·47 g.) in ethanol (200 ml.) for 12 hr. The solvent was removed *in vacuo* and the crude red product was chromatographed as before. Four bands developed. The first two, bright yellow and red respectively, were washed from the column with benzene and the last two, also bright yellow and red respectively, were removed separately from the dried column and were washed from the alumina with ethanol or acetone. The solid component from each band was isolated by evaporation of the solvent *in vacuo*.

Band 1 gave 3-ethoxy-2,4,5-trifluoro-6-nitroaniline (VIII) (0·05 g.), m. p. 73—73·5° [from benzene–light petroleum (b. p. 60—80°)], unchanged on admixture with an authentic specimen; it also had an identical infrared spectrum.

Band 2 gave the diamine (III) (0·05 g.), m. p. 135—159°. Recrystallisation from light petroleum (b. p. 60—80°)–benzene gave the pure compound (0·01 g.), m. p. 157—163·5° (i.r.).

Band 3 gave the diamine (V) (0·3 g.), m. p. 146—148° (i.r.).

Band 4 gave almost pure triamine (VI) (0·01 g.), m. p. 221—228° (i.r.).

A red band followed band 2, but only a tar (0·006 g.) was isolated from it.

(b) 2,3,5,6-*Tetrafluoro*-4-*nitroaniline* (IV). The compound (0·50 g.), ethanol (4·0 ml.), and aqueous ammonia (2·0 ml.; *d* 0·88) were left at room temperature for 90 hr. The solution was diluted with ether, dried ($MgSO_4$), and evaporated *in vacuo*, to leave a red residue which was separated into three bands on alumina as before.

Band 1 gave almost pure starting material (0·09 g.), m. p. 101—106° (i.r.).

Band 2 gave the diamine (V) (0·39 g.), m. p. 143—146°. The pure compound (0·27 g.), m. p. 147—148° (from benzene), had an infrared spectrum identical with that of the compound prepared previously.

Band 3 afforded almost pure triamine (VI) (0·01 g.) (i.r.).

3-*Ethoxy*-2,4,5-*trifluoro*-6-*nitroaniline* (VIII).—A solution of the amine (II) (0·09 g.) in ethanol (32 ml.) was treated with 0·053N-ethanolic sodium ethoxide (8·0 ml.) for 18 hr. at room temperature. Evaporation *in vacuo* left a bright yellow solid, which yielded only one band on alumina. It crystallised from benzene–light petroleum (b. p. 60—80°), to give the *ether* (VIII) (0·05 g.), m. p. 73—73·5° (Found: C, 41·0; H, 3·1. $C_8H_7F_3N_2O_3$ requires C, 40·7; H, 3·0%).

2,4-*Difluoro*-6-*nitrobenzene*-1,3,5-*triamine* (VI).—The nitro-amine (IV) (0·5 g.), ethanol (4·0 ml.), and aqueous ammonia (2·0 ml.; *d* 0·88) were heated together in a sealed tube at 110° for 4 hr. The tube was allowed to cool and the deep red crystals which separated out were redissolved with acetone. Evaporation of the dried ($MgSO_4$) solution left a residue (0·51 g.), m. p. 210—215°. Recrystallisation of a small sample of this from ethanol–acetone, followed by sublimation at 190°/0·05 mm., gave the *triamine*, m. p. 230·5—231° (Found: C, 35·2; H, 3·2; F, 18·8. $C_6H_6F_2N_4O_2$ requires C, 35·3; H, 3·0; F, 18·6%). A M-solution in acetone had a single sharp peak in the nuclear magnetic resonance spectrum at 94·7.

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Treatment of the Trifluoronitrophenylenediamines (III *and* V) *with Aqueous-ethanolic Ammonia.*—(*a*) The compound (V) (24 mg.), ethanol (4·0 ml.), and aqueous ammonia (2·0 ml.; *d* 0·88) were heated together in a sealed tube at 135° for 7¾ hr. The crude product, isolated as in the previous experiment, gave only one band on alumina with benzene as eluant. This was washed from the column with acetone, and the acetone was evaporated to leave the triamine (VI) (22 mg.), m. p. 229—231° (i.r.).

(*b*) Compound (III) (22 mg.), treated as in (*a*), gave almost pure triamine (VI) (15 mg.), m. p. 198—207° (i.r.)

Hydrogenation of 2,3,4,5-*Tetrafluoro*-6-*nitroaniline* (II).—The compound (3·79 g.), m. p. 38—40°, was hydrogenated in ethanol over Raney nickel for 18 hr. at atmospheric pressure and room temperature (uptake about 1·3 l.). After filtration and evaporation the residue (3·05 g.), m. p. 125—129°, was sublimed at 110° *in vacuo* and then recrystallised from benzene, to give 3,4,5,6-*tetrafluoro*-1,2-*phenylenediamine* (2·15 g.), m. p. 131—131·5° (Found: C, 40·2; H, 2·2. $C_6H_4F_4N_2$ requires C, 40·0; H, 2·2%). Infrared spectroscopy showed that this compound was different from 2,4,5,6-tetrafluoro-1,3-phenylenediamine reported [2] previously. A 3M-solution in acetone had two, identical, bands at 87·1 and 99·3 in the nuclear magnetic resonance spectrum.

A rapid stream of carbonyl chloride was passed through a solution of the diamine (0·14 g.) in dry ether for 1 min. A white precipitate of 4,5,6,7-tetrafluoro-2,3-dihydro-2-benzimidazolone (0·14 g.), m. p. 302·5—306°, was formed almost immediately: it had an infrared spectrum identical with that of a specimen prepared [5] by an alternative route.

The diamine (0·5 g.) was refluxed for 2 hr. with trifluoroacetic anhydride (3·0 ml.) and two drops of concentrated hydrochloric acid. The excess of anhydride was removed by co-distillation with carbon tetrachloride, and the solid residue was refluxed for 30 min. with water. Excess of aqueous ammonia (*d* 0·88) was added and the solution was allowed to cool. A solid (0·4 g.) separated and was recrystallised from light petroleum (b. p. 80—100°) containing a small amount of benzene, to give 4,5,6,7-*tetrafluoro*-2-*trifluoromethylbenzimidazole* (0·21 g.), m. p. 163—163·5° (Found: C, 37·2; H, 0·2. $C_8HF_7N_2$ requires C, 37·2; H, 0·4%), $\lambda_{max.}$ (in EtOH) 228 and 248 mμ (ε 4400 and 4800, respectively), $\lambda_{infl.}$ 267 mμ (ε 3400).

Cyanogen bromide (0·93 g.) was added slowly, with shaking, to a suspension of the 1,2-diamine (1·0 g.) in water (10 ml.). After being shaken for 18 hr. at room temperature the clear brown solution was made alkaline with aqueous ammonia (*d* 0·88). The white precipitate (1·20 g.), m. p. 278·5—282·5°, was filtered off and recrystallised from aqueous ethanol to give 2-*amino*-4,5,6,7-*tetrafluorobenzimidazole* (0·52 g.), m. p. 289—290·5° (Found: C, 41·1; H, 1·6. $C_7H_3F_4N_3$ requires C, 41·0; H, 1·5%).

Hydrogenation of 2,3,5,6-*Tetrafluoro*-4-*nitroaniline* (IV).—This compound (1·96 g.) was hydrogenated in the same way as the isomer (II) (uptake about 700 ml.). The product was 2,3,5,6-*tetrafluoro*-1,4-*phenylenediamine* (1·30 g.), m. p. 143·5—144° (Found: C, 40·2; H, 2·4%). Infrared spectroscopy showed that this compound differed from the isomeric 1,2- and 1,3-diamines. Nuclear magnetic resonance spectroscopy of a 2M-solution in acetone showed a single sharp peak at 86·7.

Treatment of the *p*-diamine (0·25 g.) with trifluoroacetic anhydride (2·0 ml.) gave the *bistrifluoroacetyl derivative* (0·34 g.), m. p. 274·5—275° (from aqueous ethanol) (Found: C, 32·0; H, 0·4. $C_{10}H_2F_{10}N_2O_2$ requires C, 32·3; H, 0·5%).

Hydrogenation of 2,4,5-*Trifluoro*-6-*nitro*-1,3-*phenylenediamine* (V).—This compound (4·45 g.) was hydrogenated as before to give 3,5,6-*trifluorobenzene*-1,2,4-*triamine* (VII) (1·3 g.), m. p. 164° (decomp.) (from benzene–ethanol) (Found: C, 40·7; H, 3·6. $C_6H_6F_3N_3$ requires C, 40·7; H, 3·4%). The nuclear magnetic resonance spectrum of a 5M-solution in acetone showed three equal bands at 82·4, 87·3, and 95·0.

Nuclear Magnetic Resonance Measurements.—These were carried out on a Mullard SL 44 Mark 1 instrument at 30·107 Mc./sec. The figures quoted are fluorine chemical shifts and are in p.p.m. from trifluoroacetic acid as external reference.

We thank Dr. L. F. Thomas and Mr. J. Homer for the magnetic measurements and the Wellcome Trust for a grant (to G. M. B.).

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[*Received, August 8th,* 1960.]

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173. *Aromatic Polyfluoro-compounds. Part VIII.*[1] *Pentafluorobenzaldehyde and Related Pentafluorophenyl Ketones and Carboxylic Acids.*

By A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow.

Pentafluorophenylmagnesium halides with *N*-methylformanilide or ethyl formate gave pentafluorobenzaldehyde. This was converted into 2,3,4,5,6-pentafluoro-benzoic, -mandelic, -cinnamic, and -phenylpropionic acid. Reduction gave 2,3,4,5,6-pentafluorobenzyl alcohol which was converted into 2,3,4,5,6-pentafluorobenzyl chloride and bromide. These were prepared also from 2,3,4,5,6-pentafluorotoluene, made both from pentafluorophenylmagnesium iodide and dimethyl sulphate, and from hexafluorobenzene and methyl-lithium. The benzyl halides gave the cyanide and thence pentafluorophenyl-acetic acid, -ethanol, and -ethylamine. 2,3,4,5,6-Pentafluorotoluene gave 2,3,5,6-tetrafluoro-*p*-xylene on further reaction with methyl-lithium. From pentafluorophenylmagnesium halides, dimethyl(pentafluorophenyl)methanol (and thence 2,3,4,5,6-pentafluoro-α-methylstyrene), bispentafluorophenylmethanol (and thence decafluorobenzophenone), α-pentafluorophenylbenzyl alcohol (and thence 2,3,4,5,6-pentafluorobenzophenone), 2,3,4,5,6-pentafluoroacetophenone, and octafluoroacetophenone were made. Haloform cleavage of the last gave pentafluorobenzene and trifluoroacetic acid.

Previous preparations [2] of pentafluorobenzaldehyde from pentafluorophenylmagnesium bromide and ethyl orthoformate or 3,4-dihydro-6-methyl-3-*p*-tolylquinazoline methiodide gave poor yields. Better routes have now been found in the reactions of this or the analogous iodo-Grignard reagent with an excess of ethyl formate [3] or of *N*-methylformanilide.[4] From the former, pentafluorobenzaldehyde was prepared in about 40% yield, bispentafluorophenylmethanol being formed as well (see below). By the latter route, yields of aldehyde were about 60%, and there was no evidence of amine formation as is the case with phenylmagnesium bromide.[4] Pentafluorobenzaldehyde, a low-melting solid, did not give a hydrate very readily but formed derivatives, *e.g.*, *N*-(2,3,4,5,6-pentafluorobenzylidene)aniline and 2,3,4,5,6-pentafluorobenzylidene diacetate in the normal way. The aldehyde did not appear to undergo atmospheric oxidation particularly rapidly, though, when oxygen was bubbled through it at 110°, pentafluorobenzoic acid [2,5] was formed. This oxidation was also done with sodium dichromate, the acid being characterised by conversion into its acid chloride and then into amides. The reaction of the aldehyde bisulphite compound with potassium cyanide has been repeated and (±)-2,3,4,5,6-pentafluoromandelic acid obtained by hydrolysis of the nitrile [2] *in situ*.

Application of the Perkin and the Knoevenagel reaction to pentafluorobenzaldehyde gave 2,3,4,5,6-pentafluorocinnamic acid. In the former process a lower temperature (130°) than that usually recommended gave a larger yield. The use of piperidine in the Knoevenagel reaction was not necessary. However, the initial product of the reaction, a viscous liquid, appeared to consist largely of a hydroxy-acid, which nevertheless gave the cinnamic acid on treatment with concentrated sulphuric acid. Presumably, the strongly electron-withdrawing pentafluorophenyl group stabilizes the hydroxyl group on $C_{(2)}$ of the side chain (cf. *p*-nitrobenzaldehyde and hydantoin,[6] and aliphatic fluoro-aldehydes [7]). The strong selective ultraviolet absorption suggests that the acid obtained is very largely

[1] Part VII, Brooke, Burdon, and Tatlow, preceding paper.
[2] Nield, Stephens, and Tatlow, *J.*, 1959, 166.
[3] Gattermann and Maffezzoli, *Ber.*, 1903, **36**, 4152.
[4] Smith, and Bayliss, *J. Org. Chem.*, 1941, **6**, 437.
[5] McBee and Rapkin, *J. Amer. Chem. Soc.*, 1951, **73**, 1366.
[6] Phillips, and Murphy, *J. Org. Chem.*, 1951, **16**, 954.
[7] McBee, Roberts, and Wilson, *J. Amer. Chem. Soc.*, 1957, **79**, 2323.

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the *trans*-isomer.[8] This acid was hydrogenated smoothly over Raney nickel to give β-(2,3,4,5,6-pentafluorophenyl)propionic acid.

As expected, pentafluorobenzaldehyde did not undergo a Cannizzaro reaction with aqueous alkali. Instead, a haloform cleavage, typical of fluoro-carbonyl compounds, occurred to give pentafluorobenzene and formic acid.

Pentafluorobenzaldehyde was readily reduced by lithium aluminium hydride in diethyl ether at 20°, to 2,3,4,5,6-pentafluorobenzyl alcohol, which formed esters in the usual way. This alcohol, which has already been reported [5] in crude form as the reduction product of pentafluorobenzoic acid, was made also by treatment of 2,3,4,5,6-pentafluorobenzyl chloride (see below) with potassium carbonate solution. It was converted into 2,3,4,5,6-pentafluorobenzyl bromide with hydrogen bromide and into the corresponding chloride by phosphorus pentachloride. The derived *S*-(2,3,4,5,6-pentafluorobenzyl)thiouronum chloride did not give a water-insoluble salt with a fluorinated dibasic acid.

Since these compounds were of potential use as intermediates, routes to them through pentafluorotoluene were investigated. Small yields of impure 2,3,4,5,6-pentafluorotoluene had been reported [9] from the reaction of hexafluorobenzene with methylmagnesium iodide. We first made it (yield 53%) from pentafluorophenylmagnesium iodide and dimethyl sulphate in ether. Better yields (70%) were obtained on reaction of hexafluorobenzene with methyl-lithium in diethyl ether, a process used also by Dr. Wall.[10] It was best to add the methyl-lithium solution to the hexafluorobenzene, but even so some 2,3,5,6-tetrafluoroxylene was formed. This compound was also obtained when 2,3,4,5,6-pentafluorotoluene was treated with methyl-lithium in ether. The orientation was established by bromination to the xylylene dibromide and oxidation of this to tetrafluoroterephthalic acid,[11] also made by hydrolysis of the side chains of perfluoro-*p*-xylene.[12] The nuclear magnetic resonance spectrum of the xylene supported this structure since four equivalent fluorine atoms were present. This is another example of nucleophilic replacement in the fluoro-aromatic field giving a *para*-product.

Bromination of 2,3,4,5,6-pentafluorotoluene to give the benzyl bromide was readily effected in ultraviolet light, and was more easily controlled than chlorination. This gave mainly 2,3,4,5,6-pentafluorobenzyl chloride but also some of the analogous benzylidene chloride and benzotrichloride. The last was hydrolysed with sulphuric acid to give pentafluorobenzoic acid. In aqueous-ethanolic solution the bromine and the chlorine in the pentafluorobenzyl halides were more susceptible than the nuclear fluorine atoms to replacement by cyanide ions (cf. sodium pentafluorobenzenesulphonate and sodium cyanide [2]). The amount of fluoride ion liberated, however, was much greater when ethanol was used as solvent. Accordingly, only sufficient ethanol was added to homogenise the system. The liquid so obtained, 2,3,4,5,6-pentafluorobenzyl cyanide, was hydrolysed by aqueous acid to give 2,3,4,5,6-pentafluorophenylacetic acid, which formed esters in the usual way. Partial hydrolysis of the nitrile gave the amide which was made also from the acid *via* the acid chloride. Reduction of ethyl 2,3,4,5,6-pentafluorophenylacetate with lithium aluminium hydride gave 2-(pentafluorophenyl)ethanol, whilst an analogous reduction of 2,3,4,5,6-pentafluorobenzyl cyanide gave pentafluorophenethylamine. The free amine decomposed on being kept, with liberation of fluoride ions, but its hydrochloride and benzoyl derivative were both stable.

With equimolar proportions of ethyl formate, or with pentafluorobenzaldehyde, pentafluorophenylmagnesium iodide gave bispentafluorophenylmethanol. Oxidation of this was difficult, but by using chromium trioxide in acetic acid there was obtained decafluorobenzophenone, the first aromatic perfluoro-ketone to be synthesised. It did not form a

[8] Braude, *Ann. Reports*, 1945, **42**, 126.
[9] Pummer and Wall, *Science*, 1958, **127**, 643.
[10] Wall, personal communication.
[11] Gething, Patrick, and Tatlow, unpublished work.
[12] Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.

hydrate readily and did not display normal carbonyl properties, for example, no oxime, semicarbazone, or 2,4-dinitrophenylhydrazone could be made. This is due presumably to steric factors (cf. 2,2′,4,4′-tetramethylbenzophenone [13]). Pentafluorophenylmagnesium bromide and benzaldehyde afforded α-pentafluorophenylbenzyl alcohol. Both this and bispentafluorophenylmethanol appeared to undergo esterification with 3,5-dinitrobenzoyl chloride in the normal manner. Presumably the presence of the pentafluorophenyl groups suppressed the tendency for alkyl–oxygen fission, a type of reaction observd [14] for diphenylmethanol and some of its substituted analogues. Oxidation of α-pentafluorophenylbenzyl alcohol with chromium trioxide in acetic acid gave 2,3,4,5,6-pentafluorobenzophenone; this was prepared also from pentafluorophenylmagnesium bromide and benzoyl chloride. This ketone formed, rather sluggishly, a 2,4-dinitrophenylhydrazone. It appeared to form an oxime also, but this decomposed rapidly, presumably by an elimination involving an *o*-fluorine atom, to give a 1,2-benzisoxazole as occurs with the oxime of 2-bromo-5-nitroacetophenone.[15]

With lithium trifluoroacetate,[16] or in poorer yield with trifluoroacetic anhydride, pentafluorophenylmagnesium iodide gave octafluoroacetophenone. This perfluoro-ketone also gave no derivatives and on its treatment with aqueous potassium hydroxide a haloform reaction occurred to give pentafluorobenzene and trifluoroacetic acid. The preferential cleavage of the aryl–carbon bond indicates a greater stability for a pentafluorophenyl than for a trifluoromethyl anion, if the reaction involves an anionic intermediate.

Pentafluorophenylmagnesium bromide and acetone gave 2,3,4,5,6-pentafluoro-αα-dimethylbenzyl alcohol, which was dehydrated easily to 2,3,4,5,6-pentafluoro-α-methylstyrene. Oxidation of this was unsuccessful, but the desired product, 2,3,4,5,6-pentafluoroacetophenone, was made from the Grignard reagent and acetyl chloride.

Experimental

Pentafluoroiodobenzene.—A mixture of penta- and hexa-fluorobenzene (84·0 g.), prepared by the defluorination of a mixture of 1*H*- and 2*H*-heptafluorocyclohexa-1,3-diene and heptafluorocyclohexa-1,4-diene,[17] was added to a stirred solution of iodine (60 g.) in sulphuric acid (20% SO_3; 100 g.) at 65—70°. After being stirred for 4½ hr. the mixture was poured on ice and decolorised with sodium hydrogen sulphite solution, and the product fractionally distilled through a 6″ vacuum-jacketed column packed with glass helices to give: (i) hexafluorobenzene (29·5 g.), b. p. 80°, (ii) a mixture of fractions (i) and (iii) (8·5 g.), and (iii) pentafluoroiodobenzene (40 g.), b. p. 162—163°.

Pentafluorobenzaldehyde.—(a) *By use of ethyl formate.* Pentafluoroiodobenzene (5·0 g.) was added to magnesium turnings (0·5 g.) in diethyl ether (25 c.c.). After reaction had been started by gentle warming, spontaneous refluxing ensued and when this ceased heat was applied for 3 hr. The solution was then added to stirred ethyl formate (10·0 g.) at 0°. After 1 hr. 5N-hydrochloric acid (100 c.c.) was added and the ether layer separated, combined with the ether extracts (2 × 50 c.c.) of the aqueous phase, dried ($MgSO_4$), filtered, and evaporated. The residual liquid was shaken with sodium hydrogen sulphite solution, and the resulting precipitate collected and decomposed by refluxing dilute sulphuric acid. The crude pentafluorobenzaldehyde so obtained was steam-distilled and the ether extract of the distillate dried, filtered, and evaporated. The liquid residue was distilled to give pentafluorobenzaldehyde (1·0 g.), m. p. 20°, b. p. 168—170°. The 2,4-dinitrophenylhydrazone [2] had m. p. and mixed m. p. 229—230°. During the steam-distillation a small amount of crystals, m. p. 74—75°, was deposited in the condenser; this was bispentafluorophenylmethanol (see below).

(b) *By use of* N-*methylformanilide.* Bromopentafluorobenzene (99·0 g.), dissolved in dry ether (50 c.c.), was added during 90 min. to magnesium turnings (10·6 g.) in dry ether (100 c.c.).

[13] Böeseken, *Rec. Trav. chim.*, 1907, **26**, 285; Cohen, *ibid.*, 1919, **38**, 119.
[14] Meisenheimer and Schmidt, *Annalen*, 1929, **475**, 177.
[15] Meisenheimer, Zimmermann, and Kummer, *Annalen*, 1925, **446**, 205.
[16] Rausch, Lovelace, and Coleman, *J. Org. Chem.*, 1956, **21**, 1328.
[17] Gething, Patrick, Tatlow, Banks, Barbour, and Tipping, *Nature*, 1959, **183**, 586.

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Further dry ether (100 c.c.) was added during the reaction. The mixture was kept at 20—25° for 16 hr., then *N*-methylformanilide (109·0 g.) was added during 100 min. The mixture was refluxed for 4 hr., then an excess of 50% v/v sulphuric acid was added, the ether distilled off, and the residue steam-distilled. The steam-distillate was extracted with ether, and the dried ($MgSO_4$) extract was filtered and evaporated. Further distillation under reduced pressure gave pentafluorobenzaldehyde (46·3 g.), b. p. 67—70°/15 mm., 168—170°/760 mm., m. p. 20° (Found: C, 42·4; H, 0·6. Calc. for C_7HF_5O: C, 42·9; H, 0·5%). There were infrared bands at 1715 and 1515 $cm.^{-1}$ attributable to carbonyl and an aromatic ring vibration, respectively.

(c) *Derivatives.* The aldehyde (1·43 g.) and aniline (0·74 g.) formed a paste. After 10 minutes' heating at 100° the solid product was collected and recrystallised from ethanol, to give N-(*2,3,4,5,6-pentafluorobenzylidene*)*aniline* (1·45 g.), m. p. 117° (Found: C, 57·7; H, 2·4; F, 34·6. $C_{13}H_6F_5N$ requires C, 57·6; H, 2·2; F, 35·0%).

Pentafluorobenzaldehyde (0·2 g.), acetic anhydride (3 c.c.), and concentrated sulphuric acid (0·1 c.c.) were kept together at 15° for 15 min. and then poured into water to give an oil which solidified (0·25 g.; m. p. 64—65°). Recrystallisation from aqueous ethanol gave *2,3,4,5,6-pentafluorobenzylidene diacetate* (0·19 g.), m. p. 64—65° (Found: C, 44·4; H, 2·3. $C_{11}H_7F_5O_4$ requires C, 44·5; H, 2·0%).

Pentafluorobenzaldehyde (2·70 g.) was shaken with an excess of saturated sodium metabisulphite solution, and the precipitated bisulphite compound (4·07 g.) collected and heated with 10% v/v sulphuric acid (40 c.c.) for 20 min. The cold solution was then extracted with ether (2 × 50 c.c.), the dried ($MgSO_4$) ether extract evaporated, and the liquid residue distilled to give pentafluorobenzaldehyde (1·42 g.), m. p. 20°, b. p. 168—170°.

Pentafluorobenzoic Acid (*with* L. J. Belf).—(*a*) A fine stream of oxygen was bubbled through pentafluorobenzaldehyde (30·6 g.) at 110° for 20 hr. Ether was added and the ethereal solution washed with an excess of sodium carbonate solution. Evaporation of the ethereal solution gave pentafluorobenzaldehyde (5·9 g.). The aqueous layer was acidified with hydrochloric acid and ether-extracted. Evaporation of the ether afforded pentafluorobenzoic acid [2] (21·1 g.), m. p. and mixed m. p. 99°.

(*b*) A mixture of pentafluorobenzaldehyde (25·3 g.), concentrated sulphuric acid (20·5 g.), sodium dichromate (15·0 g.), and water (15 c.c.) was heated at 100° for 2½ hr., then extracted with ether, and the extract was shaken with an excess of 10% sodium carbonate solution. Acidification of the aqueous layer with hydrochloric acid and extraction with ether afforded pentafluorobenzoic acid (19·8 g.), m. p. and mixed m. p. 103—104°.

2,3,4,5,6-Pentafluorobenzamide.—A mixture of 2,3,4,5,6-pentafluorobenzoic acid (8·4 g.) and phosphorus pentachloride (9·3 g.) was heated at 100° for 1 hr., then distilled to give 2,3,4,5,6-pentafluorobenzoyl chloride (5·5 g.), b. p. 60—67°/23 mm. The acid chloride (5·5 g.) in dry ether (50 c.c.), cooled in ice, was treated with an excess of gaseous ammonia. Water was added, and the ether layer, combined with ether-extracts of the aqueous phase, was washed with water, dried ($MgSO_4$), filtered, and evaporated to give *2,3,4,5,6-pentafluorobenzamide* (4·7 g.), m. p. 150° (from benzene) (Found: C, 39·7; H, 0·9. $C_7H_2F_5ON$ requires C, 39·8; H, 0·95%).

2,3,4,5,6-Pentafluorobenzoyl chloride (3·4 g.), dissolved in dry ether (50 c.c.), was cooled in ice and treated with diethylamine (2·1 g.). Water (20 c.c.) was added, and the ether layer was combined with ether extracts of the aqueous phase, washed with water, dried ($MgSO_4$), filtered, and distilled to give NN-*diethyl*-*2,3,4,5,6-pentafluorobenzamide* (3·4 g.), b. p. 128—135°/14 mm. (Found: C, 48·7; H, 3·7; F, 35·4. $C_{11}H_{10}F_5NO$ requires C, 49·4; H, 3·8; F, 35·55%).

(±)-*2,3,4,5,6-Pentafluoromandelic Acid.*—A cooled solution of potassium cyanide (1·0 g.) in water (5 c.c.) was added slowly with stirring to pentafluorobenzaldehyde sodium bisulphite compound (3·4 g.) in water (25 c.c.). After 8 hours' stirring at 15° a yellow precipitate separated and this was extracted with ether. The dried ($MgSO_4$) extract was evaporated to leave a sticky colourless gum which was kept at 100° with concentrated hydrochloric acid (50 c.c.) for 4 hr. The resulting clear solution was diluted with water and extracted continuously with ether. The ether layer was dried ($MgSO_4$), decolorised with charcoal, filtered, and evaporated to leave a white solid (1·2 g.), m. p. 141—142°, which was recrystallised twice from benzene and sublimed (90°/12 mm.) to give (±)-*2,3,4,5,6-pentafluoromandelic acid* (0·6 g.), m. p. 141—142° (Found: C, 39·8; H, 1·1. $C_8H_3F_5O_3$ requires C, 39·7; H, 1·2%), $\nu_{max.}$ 3500 and 1750 (CO_2H) and 1525 and 1515 $cm.^{-1}$ (fluorinated benzene ring) The acid (0·2 g.) and *S*-benzylthiouronium chloride gave, after two recrystallisations from water, S-*benzylthiouronium* (±)-*pentafluoromandelate* (0·1 g.), m. p. 168—169° (Found: C, 46·9; H, 2·9. $C_{16}H_{13}F_5N_2O_3S$ requires C, 47·0; H, 3·2%).

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2,3,4,5,6-*Pentafluorocinnamic Acid*.—Pentafluorobenzaldehyde (5·0 g.), acetic anhydride (4·2 g.), and fused potassium acetate (1·5 g.) were kept at 130° for 3 hr., then poured into water and the solution was made alkaline with sodium carbonate. Any unchanged aldehyde was removed by steam-distillation, and the residual liquid filtered and acidified with 16N-hydrochloric acid. The precipitate was filtered off, washed with water, dried (2·2 g.), and recrystallised from ethanol–light petroleum (b. p. 80—100°) to give 2,3,4,5,6-*pentafluorocinnamic acid*, m. p. 152·5° (Found: C, 45·3; H, 1·2. $C_9H_3F_5O_2$ requires C, 45·4; H, 1·3%), $\lambda_{max.}$ (in EtOH) 2570 Å (ε 42,000), $\nu_{max.}$ 3100—2500 and 1900 (CO_2H) and 1510 and 1530 cm.$^{-1}$ (aromatic ring). The acid (0·1 g.) and *S*-benzylthiouronium chloride gave S-*benzylthiouronium* 2,3,4,5,6-*pentafluorocinnamate* (0·07 g.), m. p. 175—176° (Found: C, 50·5; H, 3·5. $C_{17}H_{13}F_5N_2O_2S$ requires C, 50·5; H, 3·2%).

A solution of pentafluorobenzaldehyde (4·5 g.) and malonic acid (7·2 g.) in dry pyridine (10 c.c.) was kept at 100° for 90 min., then poured into 16N-hydrochloric acid at 0° and the solution extracted continuously with ether. The residual gum from the dried ether extract was kept in concentrated sulphuric acid (10 c.c.) at 100° for 10 min. and then poured on ice. The precipitate was filtered off and taken up in 5% sodium carbonate solution, and the solution was filtered and acidified to give 2,3,4,5,6-pentafluorocinnamic acid (2·4 g.), m. p. and mixed m. p. 152°.

Addition of small amounts of piperidine to the reaction mixture gave no apparent improvement. The acid (0·5 g.), neutralised with 5% sodium hydroxide solution and treated with a solution of 4-bromophenacyl bromide (0·6 g.) in ethanol at 100° for 1 hr., gave 4-*bromophenacyl* 2,3,4,5,6-*pentafluorocinnamate* (0·4 g.; from aqueous ethanol), m. p. 126·5° (Found: C, 46·7; H, 1·9. $C_{17}H_8BrF_5O_3$ requires C, 46·9; H, 1·85%).

β-(2,3,4,5,6-*Pentafluorophenyl*)*propionic Acid*.—2,3,4,5,6-Pentafluorocinnamic acid (2·2 g.) in absolute ethanol (25 c.c.), and Raney nickel (approx. 0·1 g.), were shaken in hydrogen at 20—25°/1 atm. The calculated amount was absorbed in 3 hr. The solution was filtered and the filtrate evaporated to give β-(2,3,4,5,6-*pentafluorophenyl*)*propionic acid* (1·3 g.; from water), m. p. 95—96° (Found: C, 44·8; H, 2·1. $C_9H_5F_5O_2$ requires C, 45·0; H, 2·1%).

Treated as described above, the acid (0·7 g.) afforded 4-*bromophenacyl* β-(2,3,4,5,6-*pentafluorophenyl*)*propionate* (0·6 g.; from aqueous ethanol), m. p. 111° (Found: C, 46·9; H, 2·4; F, 21·9. $C_{17}H_{10}BrF_5O$ requires C, 46·7; H, 2·3; F, 21·7%).

Reaction of Pentafluorobenzaldehyde with Aqueous Potassium Hydroxide.—Pentafluorobenzaldehyde (1·0 g.), potassium hydroxide (0·5 g.), and water (1 c.c.) were kept at 15° for 16 hr., then ether (5 c.c.) was added followed by water (5 c.c.). The aqueous layer was separated and extracted with ether. The ether was dried ($MgSO_4$) and shown by gas chromatography to contain pentafluorobenzene (0·4 g.) which was separated and found to have a correct infrared spectrum. The pH of the aqueous phase was adjusted to 4, and *S*-benzylthiouronium chloride added to give *S*-benzylthiouronium formate, m. p. and mixed m. p. 149—150°.

2,3,4,5,6-*Pentafluorobenzyl Alcohol*.—(*a*) A solution of pentafluorobenzaldehyde (10·3 g.) in dry ether (20 c.c.) was slowly added to a stirred suspension of lithium aluminium hydride (0·75 g.) in dry ether (50 c.c.) in a nitrogen atmosphere. After 90 min. at 20°, water (10 c.c.) was added slowly followed by hydrochloric acid. The ether layer was separated, the aqueous phase was extracted with ether, the combined extracts were dried ($MgSO_4$), filtered, and evaporated, and the residual liquid was distilled *in vacuo* to give 2,3,4,5,6-pentafluorobenzyl alcohol (9·7 g.), b. p. 114—115°/60 mm., 180—182°/1 atm., m. p. 30—32° (Found: C, 42·8; H, 1·8. Calc. for $C_7H_3F_5O$: C, 42·5; H, 1·6%). The alcohol (0·2 g.) and *p*-nitrobenzoyl chloride (0·2 g.) were kept together at 100° for 1 hr. and then poured into sodium hydrogen carbonate solution. The crystalline precipitate was washed with dilute hydrochloric acid and water and recrystallised from ethanol, to give 2,3,4,5,6-pentafluorobenzyl *p*-nitrobenzoate (0·3 g.), m. p. 122—123° (Found: C, 48·4; H, 1·9. Calc. for $C_{14}H_6F_5NO_4$: C, 48·4; H, 1·7%). A m. p. of 114—116° has been given [5] for this ester.

(*b*) 2,3,4,5,6-Pentafluorobenzyl chloride (3·0 g.) was boiled with potassium carbonate (5·0 g.) and water (25 c.c.) for 17 hr. The organic layer was extracted with ether, dried ($MgSO_4$), filtered, and distilled to give 2,3,4,5,6-pentafluorobenzyl alcohol (1·4 g.), b. p. 110—116°/52 mm. The alcohol (0·6 g.) in the usual way gave 2,3,4,5,6-*pentafluorobenzyl* 3,5-*dinitrobenzoate* (0·4 g.; from aqueous ethanol), m. p. 121·5° (Found: C, 42·9; H, 1·4; F, 24·2. $C_{14}H_5F_5N_2O_6$ requires C, 42·9; H, 1·3; F, 24·2%).

2,3,4,5,6-*Pentafluorobenzyl Bromide and Chloride*.—2,3,4,5,6-Pentafluorobenzyl alcohol

(1·9 g.), 48% aqueous hydrogen bromide (6 g.) and concentrated sulphuric acid (2 c.c.) were kept together at 70° for 2 hr., then poured into water (20 c.c.) and extracted with ether. The dried ($MgSO_4$) ether extract was filtered and evaporated and the residual liquid distilled to give the extremely lachrymatory **2,3,4,5,6-*pentafluorobenzyl bromide*** (0·9 g.), b. p. 174—175° (Found: C, 31·5; H, 0·8. $C_7H_2BrF_5$ requires C, 32·2; H, 0·8%).

Refluxing of the alcohol (1·5 g.) with phosphorus pentachloride (2 g.) in carbon tetrachloride (5 c.c.) for 2 hr. gave the slightly lachrymatory 2,3,4,5,6-pentafluorobenzyl chloride (1·1 g.), b. p. 160—163°. The chloride (0·5 g.) and thiourea (0·2 g.) were kept together in refluxing ethanol (10 c.c.) for 30 min. Removal of the solvent gave crystals which recrystallised from 10% hydrochloric acid gave **S-(2,3,4,5,6-*pentafluorobenzyl*)*thiouronium chloride*** (0·4 g.), m. p. 200—201° (Found: C, 32·6; H, 2·2. $C_8H_6ClF_5N_2S$ requires C, 32·8; H, 2·1%).

2,3,4,5,6-*Pentafluorotoluene*.—(a) *From the Grignard reagent.* To a stirred ethereal solution of pentafluorophenylmagnesium iodide at 0°, prepared in the usual way from pentafluoroiodobenzene (10·0 g.), was added dimethyl sulphate (8·6 g.) in dry ether (10 c.c.). When the initial reaction was complete the mixture was stirred at the b. p. for 16 hr. 5N-Hydrochloric acid (100 c.c.) was then added and the aqueous phase extracted with ether. The combined extracts were dried ($MgSO_4$) and most of the ether was distilled through a 6″ vacuum-jacketed column packed with glass helices. The residual liquid was separated by gas chromatography (column 488 × 7·5 cm.; packing dinonyl phthalate–kieselguhr 1 : 2; temp. 100°; N_2 flow-rate 52 l./hr.) to give ether, pentafluorobenzene (0·7 g.) (correct infrared spectrum), and **2,3,4,5,6-*pentafluorotoluene*** (3·3 g.), b. p. 115—118° (Found: C, 46·4; H, 1·7. $C_7H_3F_5$ requires C, 46·2; H, 1·7%), which had infrared bands at 2950, 2900, 1450, and 1380 (Me), and 1520 cm.$^{-1}$ (aromatic ring).

(b) *From hexafluorobenzene.* An ethereal solution of methyl-lithium (70 c.c., containing 2·1 g. of methyl-lithium) was added to a stirred solution of hexafluorobenzene (20 g.) in dry ether (20 c.c.) at a rate sufficient to maintain gentle refluxing. Stirring was maintained for ½ hr. after the addition was complete and water (100 c.c.) then added. The ether layer was dried ($MgSO_4$) and filtered, most of the ether distilled through a 6″ column, and the residual liquid (17 g.) separated by gas chromatography (column 488 × 7·5 cm.; packing silicone gum–kieselguhr 1 : 3; temp. 100°; N_2 flow-rate 45 l./hr.) to give ether and hexafluorobenzene (1·2 g.), 2,3,4,5,6-pentafluorotoluene (13·8 g.) (both displaying correct infrared spectra), and a fraction (2·5 g.) which was distilled to give **2,3,5,6-*tetrafluoroxylene*** (2·0 g.), b. p. 143—144° (Found: C, 53·7; H, 3·5. $C_8H_6F_4$ requires C, 53·9; H, 3·4%). The nuclear magnetic resonance spectrum indicated the presence of four equivalent fluorine atoms; there were infrared bands at 2980, 2940, 2860, and 1380 (Me) and 1495 cm.$^{-1}$ (aromatic ring).

Irradiation of the tetrafluoro-*p*-xylene (1·5 g.) and bromine (1·5 g.) with ultraviolet light at 15° for 16 hr. gave **1,4-*bisbromomethyl*-2,3,5,6-*tetrafluoroxylene*** (2·3 g.), m. p. 68—70° (Found: C, 28·8; H, 1·0. $C_8H_4Br_2F_4$ requires C, 28·6; H, 1·2%).

Oxidation of the tetrafluoroxylylene dibromide (2·0 g.) with potassium permanganate (2 g.) in the presence of sodium carbonate (2 g.) in water (50 c.c.) gave tetrafluoroterephthalic acid (0·45 g.), m. p. 283—284° alone and in admixture with an authentic specimen.[11]

2,3,5,6-*Tetrafluoroxylene from* 2,3,4,5,6-*Pentafluorotoluene*.—An ethereal solution of methyl-lithium (45 c.c.; containing 1·3 g. of methyl-lithium) was slowly added to a stirred solution of 2,3,4,5,6-pentafluorotoluene (3 g.) in ether (10 c.c.) at a rate sufficient to maintain gentle refluxing. The reaction was completed by refluxing for a further 3 hr., and the aforementioned isolation procedure gave 2,3,5,6-tetrafluoroxylene (2·5 g.) with a correct infrared spectrum.

Bromination of **2,3,4,5,6-*Pentafluorotoluene*.**—This compound (9·0 g.), mixed with bromine (8·1 g.), was irradiated with ultraviolet light at 15° for 12 hr., after which most of the bromine had reacted. The lachrymatory liquid residue was distilled from phosphorus pentoxide to give 2,3,4,5,6-pentafluorobenzyl bromide (12·0 g.), b. p. 174—175°; the infrared spectrum was identical with that of the product from the reaction of pentafluorobenzyl alcohol and hydrogen bromide [bands at 3000 (methylene) and 1510 cm.$^{-1}$ (aromatic ring)].

Chlorination of **2,3,4,5,6-*Pentafluorotoluene*.**—(*a*) A stream of chlorine was passed into boiling 2,3,4,5,6-pentafluorotoluene (50·6 g.) for 12 hr. in a silica reaction vessel irradiated with ultraviolet light. Fractional distillation of the product (57·8 g.) gave **2,3,4,5,6-*pentafluorobenzyl chloride*** (29·3 g.), b. p. 80°/47 mm., n_D^{20} 1·4435 (Found: C, 38·7; H, 1·1. $C_7H_2ClF_5$ requires C, 38·8; H, 0·9%), together with higher-boiling material (24·8 g.).

(*b*) From several experiments the last fractions were combined and fractionally distilled to

give 2,3,4,5,6-pentafluorobenzylidene dichloride, b. p. 84°/32 mm. This compound was prepared more conveniently by heating 2,3,4,5,6-pentafluorobenzaldehyde (10·6 g.) with phosphorus pentachloride (13·6 g.) at 100° for 30 min. The product was poured on ice and the organic layer dissolved in ether (50 c.c.). The ethereal solution was shaken with sodium metabisulphite solution, sodium carbonate solution, and water, and dried ($MgSO_4$). Distillation afforded 2,3,4,5,6-*pentafluorobenzylidene dichloride* (10·8 g.), b. p. 82—84°/30 mm. (Found: C, 33·4; H, 0·5. $C_7HCl_2F_5$ requires C, 33·5; H, 0·4%).

(*c*) Prolonged action of chlorine on high-boiling products (23·3 g.) arising under (*a*) gave 2,3,4,5,6-*pentafluorobenzotrichloride* (12·3 g.), b. p. 109—116°/48 mm. (Found: C, 29·8. $C_7Cl_3F_5$ requires C, 29·5%), togehter with an unidentified solid product (1·4 g.), m. p. 165°, which may have been 1,1,2,2-tetrachloro-1,2-bispentafluorophenylethane.

Hydrolysis of 2,3,4,5,6-*Pentafluorobenzotrichloride.*—2,3,4,5,6-Pentafluorobenzotrichloride (19·1 g.) was stirred and heated at 100—110° with concentrated sulphuric acid (17 c.c.), which caused vigorous evolution of hydrogen chloride. After 2 hr. the mixture was cooled and poured on ice, and the resulting aqueous solution extracted with ether. The extracts were shaken with 5% sodium hydroxide solution (150 c.c.), and the aqueous layer was acidified with sulphuric acid and extracted with ether. Evaporation afforded pentafluorobenzoic acid (13·7 g.), m. p. and mixed m. p. 100—101·5°.

2,3,4,5,6-*Pentafluorobenzyl Cyanide.*—A mixture of 2,3,4,5,6-pentafluorobenzyl chloride (11·9 g.), potassium cyanide (4·5 g.), water (15 c.c.), and ethanol (35 c.c.) was stirred at 75° for 60 min. and then poured into water (250 c.c.). The organic layer and ether extracts of the aqueous phase were combined, washed with water, dried ($CaCl_2$), filtered, and distilled to give 2,3,4,5,6-*pentafluorobenzyl cyanide* (9·0 g.), b. p. 107—111°/17 mm. (Found: C, 46·0; H, 0·9. $C_8H_2F_5N$ requires C, 46·4; H, 1·0%), $\nu_{max.}$ 2930 and 2900 (methylene), 2240 (cyanide), and 1515 cm.$^{-1}$ (aromatic ring). The same product (yield 52%) was obtained in a similar reaction with pentafluorobenzyl bromide. In both cases the aqueous phases contained fluoride ion.

2,3,4,5,6-*Pentafluorophenylacetic Acid.*—2,3,4,5,6-Pentafluorobenzyl cyanide (22·0 g.), concentrated sulphuric acid (22 c.c.), acetic acid (22 c.c.), and water (22 c.c.) were refluxed for 45 min., then poured into water. The precipitate was filtered off and taken up in sodium carbonate solution which was filtered. Acidification of the filtrate gave 2,3,4,5,6-*pentafluorophenylacetic acid* [21·0 g.; from light petroleum (b. p. 80—100°)], m. p. 109° (Found: C, 42·8; H, 1·4. $C_8H_3F_5O_2$ requires C, 42·5; H, 1·3%), $\nu_{max.}$ 3200—2500 and 1720 (CO_2H), and 1520 and 1530 cm.$^{-1}$ (aromatic ring).

2,3,4,5,6-Pentafluorophenylacetic acid (0·6 g.) with 4-bromophenacyl bromide gave 4-*bromophenacyl* 2,3,4,5,6-*pentafluorophenyl acetate* (0·7 g.; from aqueous ethanol), m. p. 104·5° (Found: C, 45·5; H, 2·0. $C_{16}H_8BrF_5O_3$ requires C, 45·4; H, 1·9%).

2,3,4,5,6-Pentafluorophenylacetic acid (11·0 g.), absolute ethanol (4·5 g.), and fluorosulphonic acid (0·5 c.c.) were boiled together for 30 min., then cooled and poured into ice-water. The organic layer and an ether extract of the aqueous layer were washed with 5% sodium hydrogen carbonate solution (25 c.c.), dried ($CaCl_2$), filtered, and distilled, finally under reduced pressure, to give *ethyl* 2,3,4,5,6-*pentafluorophenylacetate* (10·4 g.), b. p. 95—96°/14 mm. (Found: C, 47·1; H, 2·8; F, 36·9. $C_{10}H_7F_5O_2$ requires C, 47·25; H, 2·8; F, 37·4%).

2,3,4,5,6-*Pentafluorophenylacetamide.*—(*a*) A mixture of 2,3,4,5,6-pentafluorobenzyl cyanide (5·3 g.) and concentrated sulphuric acid (10 c.c.) was stirred and heated at 100° for 20 min., then poured on ice. The precipitate was washed with 5% sodium carbonate solution and water and recrystallised from ethanol–benzene to give 2,3,4,5,6-*pentafluorophenylacetamide* (2·5 g.), m. p. 187—188° (Found: C, 42·8; H, 2·2; F, 41·9. $C_8H_4F_5NO$ requires C, 42·7; H, 1·8; F, 42·2%).

(*b*) 2,3,4,5,6-Pentafluorophenylacetic acid (5·7 g.) was added to phosphorus pentachloride (5·5 g.). The reaction, initially vigorous, was completed by heating the mixture at 100° for 30 min. Distillation gave somewhat impure 2,3,4,5,6-pentafluorophenylacetyl chloride (5·1 g.), b. p. 90—95°/29 mm. The acid chloride (1·2 g.), dissolved in dry ether (30 c.c.), was cooled in ice and treated with an excess of gaseous ammonia. Then water (20 c.c.) and ether (20 c.c.) were added and, after shaking, the ether layer was separated and combined with ether extracts of the aqueous phase. The dried ($MgSO_4$) ether solution was filtered and evaporated to give 2,3,4,5,6-pentafluorophenylacetamide (1·0 g.), m. p. and mixed m. p. 187°.

The acid chloride (8·2 g.) and dry ether (100 c.c.) were cooled in ice and stirred while a solution of diethylamine (5·3 g.) in dry ether (5 c.c.) was added slowly. The mixture was

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warmed to 20—25°, then water (20 c.c.) was added to dissolve the precipitate. The ether layer, combined with an ether extract of the aqueous layer, was washed with dilute hydrochloric acid (20 c.c.), dried ($MgSO_4$), filtered, and distilled to give NN-*diethyl*-2,3,4,5,6-*pentafluorophenylacetamide* (6·3 g.), b. p. 126—128°/2 mm. (Found: C, 51·0; H, 4·4; F, 33·8. $C_{12}H_{12}F_5ON$ requires C, 51·25; H, 4·3; F, 33·8%).

2-(2,3,4,5,6-*Pentafluorophenyl*)*ethanol*.—A solution of ethyl 2,3,4,5,6-pentafluorophenyl acetate (9·8 g.) in dry ether (10 c.c.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (1·75 g.) in dry ether (70 c.c.) under dry nitrogen. Stirring was continued for 3½ hr., then the mixture was cooled in ice while water (25 c.c.) and concentrated sulphuric acid (5 c.c.) were added. The ether layer and extracts were dried ($MgSO_4$), filtered, and distilled, finally under reduced pressure, to give 2-(2,3,4,5,6-pentafluorophenyl)ethanol (7·7 g.), b. p. 104°/16 mm.

The alcohol (0·8 g.) and 3,5-dinitrobenzoyl chloride (0·8 g.) afforded 2-(2,3,4,5,6-*pentafluorophenyl*)*ethyl* 3,5-*dinitrobenzoate* (0·7 g.; from aqueous ethanol), m. p. 94—95° (Found: C, 44·8; H, 1·9; F, 22·8. $C_{15}H_7F_5O_6N_2$ requires C, 44·4; H, 1·7; F, 23·4%).

2,3,4,5,6-*Pentafluorophenethylamine*.—2,3,4,5,6-Pentafluorobenzyl cyanide (13·4 g.) in dry ether (20 c.c.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (2·5 g.) in dry ether (100 c.c.) under dry nitrogen. The mixture was stirred for 1 hr. at 20° then for 1 hr. at 30—40°. Water (15 c.c.) and 20% aqueous sodium hydroxide (4 c.c.) were added, and the ether layer was separated, dried (NaOH), filtered, and evaporated. The residue was distilled to give a light brown liquid (4·4 g.), b. p. 80—90°/20 mm., with a strong ammoniacal odour. On being kept, it became red and partly solid and was then only partially soluble in ether. The ether-insoluble part was soluble in cold water and this solution gave a positive test for fluoride ion. The clear distillate (2·5 g.) in dry ether (40 c.c.) was cooled in ice and treated with an excess of hydrogen chloride. The precipitate (2·4 g.) was recrystallised from ethanol to give 2,3,4,5,6-*pentafluorophenethylamine hydrochloride* (1·9 g.), m. p. 281° (Found: C, 39·0; H, 3·0; F, 38·9; Cl, 14·3. $C_8H_7ClF_5N$ requires C, 38·8; H, 2·85; F, 38·4; Cl, 14·3%).

The distilled amine (1·0 g.) was shaken with 10% sodium hydroxide solution (3·5 c.c.) and benzoyl chloride (0·6 c.c.). The precipitated solid was washed with water and recrystallised from aqueous ethanol to give N-*benzoyl*-2,3,4,5,6-*pentafluorophenethylamine* (0·7 g.), m. p 161—162° (Found: C, 57·3; H, 3·3; F, 30·4. $C_{15}H_{10}F_5NO$ requires C, 57·15; H, 3·2; F, 30·1%).

Bispentafluorophenylmethanol.—(*a*) Pentafluorophenylmagnesium iodide, from pentafluoroiodobenzene (5 g.), was treated with ethyl formate (1·8 g., 1 mol.) in ether (10 c.c.) in the manner described previously. Two recrystallisations of the product from perfluoro-1,4-dimethylcyclohexane gave *bispentafluorophenylmethanol* (1·2 g.), m. p. 79—80° (Found: C, 42·9; H, 0·5; F, 52·4. $C_{13}H_2F_{10}O$ requires C, 42·9; H, 0·5; F, 52·2%), $\nu_{max.}$ 3400 (OH) and 1525 cm.$^{-1}$ (aromatic ring).

(*b*) Pentafluorophenylmagnesium bromide was prepared from bromopentafluorobenzene (10·0 g.) and magnesium (1·1 g.), in dry ether (30 c.c.). After being refluxed for 3 hr., the solution was treated with pentafluorobenzaldehyde (7·6 g.) in dry ether (9 c.c.). Refluxing for 1 hr., followed by isolation as above, afforded a solid which was distilled under reduced pressure to give bispentafluorophenylmethanol (11·6 g.), b. p. 108—110°/1·5 mm., m. p. 79—80°. This alcohol (0·2 g.) and 3,5-dinitrobenzoyl chloride (0·15 g.) were refluxed together in benzene (5 c.c.) for 4 hr.; isolation as usual gave *bispentafluorophenylmethyl* 3,5-*dinitrobenzoate* (0·2 g.; from ethanol), m. p. 186—187° (Found: C, 43·4; H, 0·6. $C_{20}H_4F_{10}N_2O_6$ requires C, 43·0; H, 0·7%).

Decafluorobenzophenone.—Bispentafluorophenylmethanol (0·5 g.), chromium trioxide (2 g.) and glacial acetic acid (10 c.c.) were refluxed together for 15 min. and then poured into water. A white powder (0·3 g.), m. p. 91—92°, was obtained which was recrystallised from perfluoro-1,4-dimethylcyclohexane to give *decafluorobenzophenone* (0·1 g.), m. p. 91—92° (Found: C, 43·4. $C_{13}F_{10}O$ requires C, 43·1%), $\lambda_{max.}$ (in EtOH) 2500 Å (ε 13,000), $\nu_{max.}$ 1720 (C=O) and 1510 cm.$^{-1}$ (aromatic ring). The ketone was recovered after being refluxed for 8 hr. with 2,4-dinitrophenylhydrazine in ethanol.

α-*Pentafluorophenylbenzyl Alcohol*.—A reaction similar to (*b*) above, but with bromopentafluorobenzene (10·0 g.) and benzaldehyde (4·3 g.), afforded a colourless syrup (9·3 g.), b. p. 115—117°/1·7 mm., which crystallised (m. p. 47°) (Found: C, 56·7; H, 2·6; F, 33·9. $C_{13}H_7F_5O$ requires C, 56·9; H, 2·6; F, 34·6%); infrared bands were at 3360 (OH) and 1510 and 1525 cm.$^{-1}$ (aromatic ring).

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From 3,5-dinitrobenzoyl chloride (0·4 g.) and the alcohol (0·3 g.) in pyridine (5 c.c.) for 24 hr. at 15°, there was obtained *α-pentafluorophenylbenzyl 3,5-dinitrobenzoate* [0·2 g.; from light petroleum (b. p. 100—120°)], m. p. 139—140° (Found: C, 51·2; H, 2·0. $C_{20}H_9F_5N_2O_6$ requires C, 51·3; H, 1·9%).

2,3,4,5,6-*Pentafluorobenzophenone*.—(*a*) α-Pentafluorophenylbenzyl alcohol (0·50 g.), chromium trioxide (0·15 g.), and glacial acetic acid (13 c.c.) were stirred together for 10 hr. The mixture was poured into water, the solution was extracted with ether, the extracts were dried ($MgSO_4$) and evaporated, and the residue was distilled *in vacuo*, to give *2,3,4,5,6-pentafluorobenzophenone* (0·30 g.), b. p. 93°/0·2 mm., m. p. 33—34° (Found: C, 57·1; H, 2·1. $C_{13}H_5F_5O$ requires C, 57·3; H, 1·8%), $\lambda_{max.}$ (in EtOH) 2560 Å (ε 19,000), $\nu_{max.}$ 1704 (C=O) and 1515 cm.$^{-1}$ (aromatic ring).

(*b*) Pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (5 g.)] was added slowly at 0° to benzoyl chloride (3·0 g.) in ether (10 c.c.). After 15 hr. at 15°, isolation as before gave 2,3,4,5,6-pentafluorobenzophenone (3·4 g.).

The ketone (0·2 g.) was refluxed for 2 hr. in ethanol with 2,4-dinitrophenylhydrazine to give the *2,4-dinitrophenylhydrazone* (0·2 g.), m. p. 204—205° (from ethanol) (Found: C. 50·9; H, 2·3. $C_{19}H_9F_5N_4O_4$ requires C, 50·5; H, 2·0%).

The ketone (4·0 g.) was refluxed for 6 hr. with hydroxylamine hydrochloride (1·0 g.) and sodium acetate (1·5 g.) in ethanol (20 c.c.) and water (5 c.c.). By extraction in the usual way an oil was obtained which, on trituration with light petroleum (b. p. 60—80°) followed by recrystallisation from this solvent, gave a yellow solid (1·0 g.) which rapidly decomposed, particularly in the light.

Octafluoroacetophenone.—Pentafluorophenylmagnesium iodide (from pentafluoroiodobenzene, 5·0 g.) was added to lithium trifluoroacetate in ether [prepared by gradual addition of lithium hydride (0·136 g.) to trifluoroacetic acid (1·93 g.) in ether (10 c.c.)]. After 15 hr. at 15°, dilute sulphuric acid was added, the ether layer and ethereal extracts of the aqueous phase were dried ($MgSO_4$), and most of the ether was distilled off through a 6″ column. The residue was separated by gas chromatography [as for pentafluorotoluene (*b*)] to give ether, pentafluorobenzene (1·0 g.) and *octafluoroacetophenone* (3·2 g.), b. p. 130—131° (Found: C, 36·5. C_8F_8O requires C, 36·4%), $\nu_{max.}$ 1760 (C=O) and 1520 cm.$^{-1}$ (aromatic ring).

The same product, in smaller yield, was formed when pentafluorophenylmagnesium iodide was treated with trifluoroacetic anhydride.

No derivatives were formed when this ketone was treated with 2,4-dinitrophenylhydrazine and semicarbazide under similar conditions to those described above.

Haloform Reaction of Octafluoroacetophenone.—The ketone (1·0 g.) and 2N-aqueous potassium hydroxide (10 c.c.) were refluxed together for 4 hr. The organic layer was pure pentafluorobenzene (infrared spectroscopy). The pH of the aqueous phase was adjusted to 4 and, on addition of *S*-benzylthiouronium chloride, *S*-benzylthiouronium trifluoroacetate (0·4 g.), m. p. and mixed m. p. 174—175°, was precipitated.

2,3,4,5,6-*Pentafluoroacetophenone*.—Acetyl chloride (3·9 g.) in ether (20 c.c.) was added to pentafluorophenylmagnesium iodide (from pentafluoroiodobenzene, 5·0 g.). After 15 hr. at 15°, isolation as for the octafluorophenone afforded pentafluorobenzene (0·5 g.) and *2,3,4,5,6-pentafluoroacetophenone* (1·0 g.) (Found: C, 45·5; H, 1·4. $C_8H_3F_5O$ requires C, 45·8; H, 1·4%), $\nu_{max.}$ 2960, 1325, 1370, and 1415 (Me), 1720 (C=O), and 1505 and 1530 cm.$^{-1}$ (aromatic ring).

Pentafluoro-αα-dimethylbenzyl Alcohol.—Acetone (3·0 g.) was added to pentafluorophenylmagnesium bromide (from bromopentafluorobenzene, 5·0 g.). After 15 hr. at 15°, the product was extracted as usual and the extracts were distilled *in vacuo* to give the *alcohol* (2·7 g.), b. p. 58°/0·25 mm. (Found: C, 48·0; H, 4·5. $C_9H_7F_5O$ requires C, 47·8; H, 3·7%), $\nu_{max.}$ 3400 (OH), 2960, 2920, 1450, and 1380 (Me), and 1525 and 1495 cm.$^{-1}$ (aromatic ring).

The *3,5-dinitrobenzoate* was made in benzene–pyridine (5 : 1) at 100° for ½ hr. It had m. p. 145—146° (from ethanol) (Found: C, 45·8; H, 2·4. $C_{16}H_9F_5N_2O_6$ requires C, 45·7; H, 2·2%).

2,3,4,5,6-*Pentafluoro-α-methylstyrene*.—The last above-mentioned alcohol (1·0 g.), phosphoric oxide (3 g.), and quinol (0·1 g.) were heated together for ½ hr. at 150—160° (bath-temp.). The distillate, *2,3,4,5,6-pentafluoro-α-methylstyrene* (0·8 g.), had b. p. 144—145° and infrared bands at 2980, 2940, 2880, 1446, and 1333 (Me and methylene), and 1528 and 1502 cm.$^{-1}$ (aromatic ring) (Found: C, 51·4; H, 2·6. $C_9H_5F_5$ requires C, 51·7; H, 2·9%).

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The authors thank Professor M. Stacey, F.R.S., and Mr. A. J. Edwards for their interest, the University for a scholarship (to P. L. C.), and Dr. K. J. Morgan for infrared spectroscopy.

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174. *Co-ordination Compounds having Carboxylic Esters as Ligands. Part I. Stoicheiometry, Structure, and Stereochemistry.**

By M. F. LAPPERT.

1 : 1 Addition compounds of ethyl acetate with some Group III and Group IV (2 : 1 for SnX_4) halides, iron(III) chloride (2 : 1), and a number of organoboron halides have been prepared. The infrared carbonyl stretching vibrations are lowered in frequency but increased in intensity, and the C_{Acyl}–O and CH stretching frequencies are increased, relatively to those in ethyl acetate. These data require structure (I) for the complexes, *i.e.*, acyl-oxygen is the donor atom. The relative donor strengths of carboxylic esters are discussed, as is the stereochemistry of the complexes. Nuclear magnetic resonance spectra of aluminium bromide–ethyl acetate and of acetone–boron trifluoride are described.

THE existence of complexes between carboxylic esters and inorganic electron-deficient halides has been known since Demarçay's preparation in 1873 of the 1 : 1 adduct of titanium(IV) chloride and ethyl acetate.[1] Complexes of the following Group III and IV halides have been reported: boron trifluoride [2-5] and trichloride,[6] tin(IV) chloride [7-12] and bromide,[7,12] titanium(IV) chloride,[1,8,13,14] and zirconium(IV) chloride,[15-17] bromide,[18] and iodide.[19] These were all 1 : 1 complexes except the tin and zirconium compounds which preferentially formed with 2 mols. of ester. Iron(III) chloride formed a 1 : 1 adduct with ethyl cinnamate.[7]

Physicochemical investigations have been concerned with measurements of electrical conductance,[2,12,13] viscosity,[3b,12,13] dipole moment,[8,16-19] surface tension and parachor,[4]

* For preliminary results see Internat. Conference on Co-ordination Chemistry, London, 1959, *Chem. Soc. Spec. Publ.*, No. 13, p. 179.

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[2] Greenwood and R. L. Martin, *J.*, 1953, 751.
[3] Greenwood and R. L. Martin, (*a*) *J.*, 1953, 1427; (*b*) *J.*, 1951, 1795; (*c*) *Proc. Roy. Soc.*, 1952, *A*, **215**, 46.
[4] Sugden and Waloff, *J.*, 1932, 1492.
[5] Greenwood and R. L. Martin, *Quart. Rev.*, 1954, **8**, 1; Morgan and Taylor, *J. Soc. Chem. Ind.*, 1931, **50**, 869; *J.*, 1932, 1497; Bowlus and Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835.
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[14] Bradley, Hancock, and Wardlaw, *J.*, 1952, 2773; Scagliarini and Tartarini, *Atti Accad. naz. Lincei, Rend. Classe Sci. fiz. mat. nat.*, 1926, **4**, 318; Hertel and Demmer, *Annalen*, 1932, **499**, 134.
[15] Bradley, Abd-El Halim, and Wardlaw, *J.*, 1950, 3450; Rosenheim and Hertzmann, *Ber.*, 1907, **40**, 810.
[16] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1957, **27**, 2921.
[17] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1959, **29**, 1375.
[18] Kletenik and Osipov, *Zhur. obshchei Khim.*, 1959, **29**, 1423.
[19] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1959, **29**, 2119.

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density,[3c,10,13] dielectric permeability,[17] specific heat,[12] heat of mixing,[11,17] and transport of ions during electrolysis.[3a,9] Little work has been done on the chemical behaviour of the ester complexes, except with those of boron trichloride,[6] which were shown to decompose either by acyl–oxygen (if R in $R'\cdot CO_2R$ was a primary alkyl or an aryl group) or alkyl–oxygen fission.

The original suggestion about the structure of the complexes was that acyl-oxygen was the donor atom in tin(IV) chloride derivatives, because these, like ketone and aldehyde but unlike ether adducts, were of 1 : 2 stoicheiometry.[7] Alkyl–oxygen donation was proposed for boron trifluoride–ethyl acetate, because its stability appeared to be comparable with that of ether–trifluoride complexes (but different from that of aldehyde and ketone adducts).[20] Ionic self-dissociation for the same molten compound was interpreted in terms of $Et^+[BF_3,Me\cdot CO_2]^-$,[21] but this was excluded by the results of electrolysis and structures $H^+[BF_3,Me\cdot CO_2C_2H_4]^-$ and $[CH_3\cdot CO]^+[BF_3\cdot OEt]^-$ were instead proposed.[3a]

Donor properties of the alkoxycarbonyl group in metal chelates have long been recognised, *e.g.*, in derivatives of ethyl acetoacetate and methyl salicylate, and in some cases, *e.g.*, $R_2B\cdot O\cdot CMe{:}CH\cdot CO_2Et$,[22] it has been shown that acyl-oxygen is the donor atom.

Hydrogen-bonding with carboxylic esters has also been studied. In the enol form of ethyl acetoacetate, it is acyl-oxygen which is the donor atom.[23] This was also believed to be the case in ethanolic ethyl acetate; the evidence was a small (9 $cm.^{-1}$) decrease in the carbonyl stretching frequency, as between the ester in ethanol and the free ester,[24] and a high value for the association constant (as in ethanolic acetic anhydride).[25] On the other hand, in certain steroid hydroxy-esters, alkyl-oxygen was the donor atom.[26] In discussion of mechanism for fission of certain carboxylic esters the formation of adducts with the alkyl-oxygen atom as donor has been postulated (*i.e.*, $R'\cdot CO_2R,H^+$ in acid-catalysed hydrolyses and transesterifications,[27] $Ar\cdot CO_2R,AlCl_3$ in the Fries rearrangement,[28] and $R'\cdot CO_2R,BH_3$ in the diborane–ester reaction [20]).

Our work had the following objects: (i) to determine the range of compounds which co-ordinate with carboxylic esters and to establish the stoicheiometry of the adducts; (ii) to obtain at least a qualitative indication of the donor strengths of carboxylic esters relative to other common ligands (particularly those in which an oxygen atom is the donor); (iii) to establish the structure and stereochemistry of the adducts; (iv) to measure spectroscopically the relative acceptor strengths of Lewis acids (with an ester as reference base) and the transmission of electronic effects through atoms other than carbon in electron-deficient compounds; and (v) to apply the results [particularly of (iii)] to the mechanism of reactions of carboxylic esters. The present paper deals with matters (i)—(iii); the others will be considered in later Parts.

Our experiments were with complexes of ethyl acetate and the following: boron trifluoride, trichloride, and tribromide, aluminium chloride and bromide, tin(IV) chloride and bromide, gallium(III), indium(III), titanium(IV), iron(III), and some organoboron chlorides. These were all 1 : 1 complexes, except for the tin and iron compounds which had 2 mol. of ligand. Most of them were prepared by interaction of equimolar proportions in pentane, the complex being precipitated [this method failed for the tin bromide and di-n-butylboron chloride complexes (see below) and was inapplicable to others (complexes

[20] Brown, Schlesinger, and Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.
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[22] Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, *J.*, 1958, 3652; Gerrard, Lappert, and Shafferman, *Chem. and Ind.*, 1958, 722.
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[28] Baltzly, Ide, and Phillips, *J. Amer. Chem. Soc.*, 1955, **77**, 2522.

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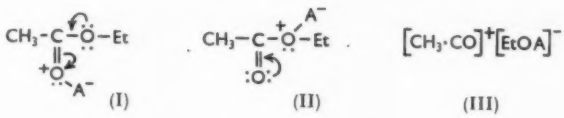
of AlX_3, $GaCl_3$, $InCl_3$, and $FeCl_3$)]. The remaining compounds were prepared in absence of solvent and invariably (except $InCl_3$) mixing was exothermal. The indium chloride adduct was prepared by heating the chloride with an excess of ethyl acetate and evaporation of solvent from the supernatant liquor. The aluminium chloride complex was also prepared by metathesis between the diethyl ether complex and ethyl acetate. All the complexes were low-melting white solids, except for the titanium (yellow) and iron (rust-coloured) chloride adducts.

Silicon(IV) and germanium(IV) chloride did not react with ethyl acetate: there was no heat of mixing and spectroscopic examination (see Part II) showed only slight association, even at −180°.

Ethyl acetate and tin bromide were miscible in pentane and spectroscopic examination showed slight association between them; di-n-butylboron chloride behaved similarly. Thus the tin bromide and di-n-butylboron chloride complexes are the least stable of those described. The next in order of instability appears to be that of diphenylboron chloride, because its dissociation vapour pressure at 20° was sufficiently large for ethyl acetate to be slowly removed at 0·1 mm.

Infrared Spectra and Structure of the Complexes.—In the light of previous suggestions, three structures (I—III) require consideration (A denotes the acceptor molecule).



(I) (II) (III)

The effect of acyl–oxygen donation (I) would be to lengthen the C=O bond and shorten the contiguous acyl C–O bond (the O–alkyl-C bond would probably be slightly lengthened). The effect of alkyl-oxygen donation (II) would be the reverse. The acetylium ion in (III) would have considerable triple bond character ($CH_3{\cdot}C^+{=}O \longleftrightarrow CH_3{\cdot}C{\equiv}O^+$) and thus the carbonyl bond would be much shortened. These bond-length changes refer to the situation in the free ester as standard. It is to be expected, from simple Hooke's law considerations, that these bond-length changes would be reflected in the appropriate bond vibration stretching frequencies (*i.e.* bond lengthening by decrease in the stretching frequency, and conversely). That this assessment is correct, at any rate for the carbonyl group, is evident since the bond length of a carbonyl group increases with polarity,[29] the vibration stretching frequency is a direct function of the bond length,[30] and in molecules XYC=O there is a linear relation between the sum of the electronegativities of X and Y and the carbonyl stretching frequency.[31] Moreover, in esters $R'{\cdot}CO_2R$ (where R and R′ are alkyl groups) the carbonyl stretching frequency generally lies at about 1740 cm.$^{-1}$ and this value is increased or decreased, depending on whether the groups R and R′ are electron-attracting or releasing.[32] Finally, in co-ordination compounds of carbonyl compounds, such as aldehydes and ketones, where there is no ambiguity regarding the carbonyl-oxygen's being the donor atom, a substantial decrease (50—150 cm.$^{-1}$) in the carbonyl stretching frequency in the complex relative to that in the free ligand has been observed.[33]

The suggestion that bond-length changes would be reflected in the observed vibration frequencies ignores the kinematic coupling effects between the two oscillators C–O and O–A. Thus, in structure (I) for example, this effect would give rise to a slight rise in the carbonyl stretching frequency, but a precise estimate would require knowledge of the

[29] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 561.
[30] Margoshes, Filtwalk, Fassel, and Rundle, *J. Chem. Phys.*, 1954, **22**, 381.
[31] Karagise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[32] Thompson and Torkington, *J.*, 1945, 640; Rappaport, Hampton, and Newell, *Analyt. Chem.*, 1949, **21**, 914.
[33] Cassimatis and Susz, *Helv. Chim. Acta*, 1960, **43**, 852, and previous papers by Susz.

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C–O and O–A stretching force constants (such an estimate has been made for the P=O vibration frequency in phosphine oxide complexes [34]).

The infrared spectra of all the complexes were investigated. The principal changes, compared with the spectrum of ethyl acetate,[35] were: (i) the carbonyl stretching frequency decreased from 1741 in ethyl acetate to between 1656 ($FeCl_3$, the highest value) and 1548 cm.$^{-1}$ (BBr_3, the lowest value); (ii) the stretching frequency of the C–O group contiguous to the carbonyl group increased from 1240 in the ester to between 1300 ($FeCl_3$, the lowest value) and 1350 cm.$^{-1}$ (BBr_3, the highest value); (iii) the stretching frequency of the C–O group contiguous to the ethyl group decreased from 1047 in the ester by 5—20 cm.$^{-1}$; (iv) the CH stretching frequencies at 2940 and 2896 cm.$^{-1}$ in ethyl acetate increased by 20—40 cm.$^{-1}$; (v) changes appeared in the CH deformation frequencies; (vi) the intensities of the carbonyl stretching frequency and of the CH deformation frequencies considerably increased in the complexes. Observations (i)—(iii) are precisely those predicted for structure (I) which is also consistent with (vi); thus carbonyl intensities increase also in solvents of high polarity.[36] As all the complexes qualitatively showed the same changes, the comparisons with ethyl acetate of only two are detailed in the Table and in the Figure. Quantitative aspects will be considered in Part II.

Infrared spectra frequencies (cm.$^{-1}$) *of ethyl acetate and two complexes.**

$CH_3{\cdot}CO_2Et$ (liquid)	$(CH_3{\cdot}CO_2Et)_2,SnCl_4$ (liquid)	$CH_3CO_2Et,AlCl_3$	Assignment †
2940 (1)	2967 (1)	2976 (1)	νCH_3
2896 (2)	2930 (2)	2941 (2)	νCH_2
1741 (3)	1613 (3)	1622 (3)	$\nu C{=}O$
1475 (4)	1470 (4)	1475 (4)	
1464 (5)	1422 (5)	1439 (5)	
1450 (6)	1383 (6)	1389 (6)	
1396 (7)			
1374 (8)			
1300 (9)			
1268 (10)	1285 (8)	1250 (8)	
1240 (11)	1319 (7)	1332 (7)	ν(CO–O)
1112 (12)	1111 (9)	1156 (9)	
		1114 (10)	
1096 (13)	1098 (10)	1098 (11)	
1047 (14)	1040 (11)	1042 (12)	νC–O(–Et)
1004 (15)	1004 (12)	1004 (13)	
937 (16)	850 (13)	983 (14)	
917 (17)		852 (15)	
847 (18)		806 (16)	

* Numbers in parentheses refer to the Figure.
† Assignments based on ref. 35 and Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201.

Structure (III) would require the presence of the carbonyl stretching frequency at ~2190 cm.$^{-1}$ (this has been shown to be characteristic for the acetylium ion in $[CH_3{\cdot}CO]^+[BF_4]^-$ [37]) and may therefore be discounted.

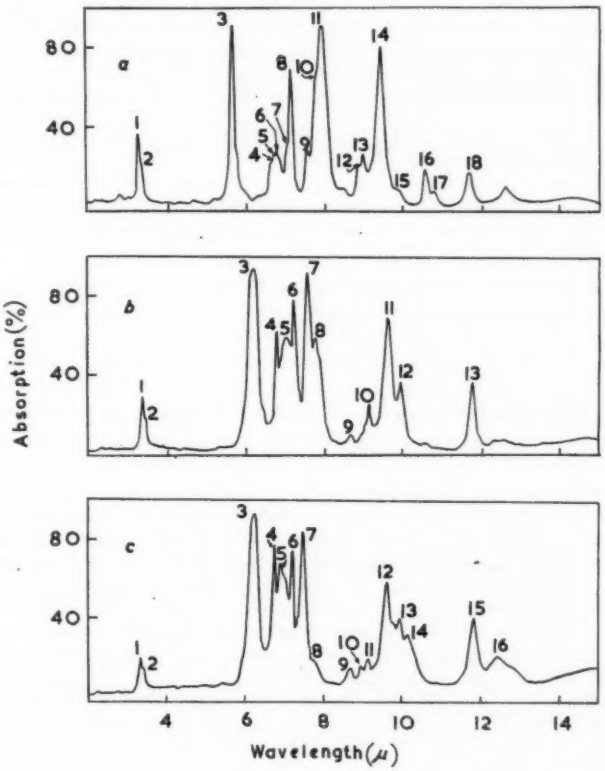
The Donor Strength of Ethyl Acetate.—That the ester displaced diethyl ether from its complex with aluminium chloride indicates that it is the stronger donor. Among carbonyl compounds, on the assumption that esters donate through the acyl-oxygen atom, it would be predicted that donor strengths would decrease in the series Me·CO·OEt > Me·CO·R > Me·CO·H, because of the possibility of mesomeric and inductive effects in the first two cases. Data are not available for such a series, but the shifts in carbonyl stretching frequency of some ketone–boron trifluoride complexes (acetone 70 cm.$^{-1}$; acetophenone 107 cm.$^{-1}$; benzophenone 112 cm.$^{-1}$) may be compared with that (119 cm.$^{-1}$) for ethyl acetate–boron trifluoride: such a comparison appears reasonable because kinematic coupling is

[34] Cotton, Barnes, and Bannister, *J.*, 1960, 2199.
[35] Nolin and Jones, *Canad. J. Chem.*, 1956, **34**, 1392.
[36] Archibald and Pullin, *Spectrochim. Acta*, 1958, **12**, 34.
[37] Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 971.

likely to be similar in all cases. Qualitative comparisons of donor properties [with antimony(v) chloride as reference acid] between acetone and ethyl acetate, by differential thermochemistry, indicate that the latter is the stronger donor.[38]

Stereochemistry of the Complexes.—On the basis of structure (I), the carbonyl-oxygen atom may, in simplified terms, be considered as having sp^2-hybridised bond orbitals, with the remaining p_z-electrons involved in π-bonding. The angle $\angle$COA approximates to 120° and the possibility is that *cis*- and *trans*-isomers may exist owing to restricted rotation about a C=O bond. Accordingly, the proton nuclear magnetic resonance spectrum of the aluminium bromide complex was compared with that of ethyl acetate. In ethyl acetate,

Infrared spectra of (a) *ethyl acetate* (*liquid*), (b) $(CH_3{\cdot}CO_2Et)_2,SnCl_4$ (*liquid*), *and* (c) $CH_3{\cdot}CO_2Et,AlCl_3$.



bands due to the protons of the acyl-methyl group (i) and the methylene group (ii) were at 0·76 and 2·88 p.p.m., respectively, both on the low-field side of band (iii) which arises from protons of the alkyl-methyl group. In the complex, examined as a solution in benzene, bands (i) and (ii) were separated by 0·99 and 2·37 p.p.m., respectively from band (iii). That on complex-formation there should be chemical shifts in opposite directions for the two sets of protons is surprising and no clear interpretation appears possible.

For the complex of acetone and boron trifluoride there should, on the above argument, be a chemical shift between the two sets of methyl-protons, as one methyl group would be *cis* and the other *trans* to the acceptor. However, even when the complex, dissolved

[38] Linqvist and Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

in methylene dichloride, was cooled to −70°, the spectrum showed merely one sharp band, which was on the low-field side at 0·975 p.p.m., against cyclohexane as internal reference. This may be compared with a band on the low-field side at 0·655 p.p.m. for acetone; the shift to the lower field in the complex may be accounted for by the electron-demand made on the methyl groups in co-ordinated acetone. The failure to demonstrate a chemical shift between the two sets of protons in the complex is not necessarily due to angle COB's being 180° and indeed is more likely due to rapid exchange of boron trifluoride among donor molecules, as has been demonstrated for trifluoride–alcohol adducts.[39]

Experimental.—The complexes were prepared as already described. The ratio donor : acceptor was established gravimetrically and confirmed by analysis for halide ion (Volhard) on hydrolysed samples.

Infrared spectroscopic measurements were taken on a Grubb–Parsons S3A double-beam spectrometer with rock-salt optics and calibrated throughout its range by using water, ammonia, and carbon dioxide as standards. Samples were studied as pure materials or (BBr_3, $TiCl_4$, $FeCl_3$) as solid mulls in both liquid paraffin and hexachlorobutadiene. With tin(IV) bromide–ethyl acetate, the pentane solution was also examined in a low-temperature cell with a variable path length.

Nuclear magnetic resonance spectra were obtained at 40 Mc./sec. on a Varian Associates model 4300B spectrometer.

The author is indebted to Mr. H. Pyszora and Dr. L. Pratt for the infrared and nuclear magnetic resonance spectral measurements, respectively, and to Dr. L. A. Duncanson for valuable discussions.

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[39] Diehl and Gränacher, *Helv. Phys. Acta*, 1958, **31**, 43.

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175. *The Mechanism of Protodeiodination of* p-*Iodoaniline.*

By H. S. CHOGUILL and J. H. RIDD.

The rate of protodeiodination of *p*-iodoaniline in aqueous solutions of mineral acids (0·025—6·0M) is shown to be of first order with respect to the stoicheiometric concentration of *p*-iodoaniline, but independent of the concentration of hydrogen ions and of iodide ions. The rate in aqueous solutions is greater than that in deuterium oxide by a factor of about 6. These results indicate: (1) that the transition state for deiodination is similar to that for the uncatalysed mechanism of iodination at lower acidities where the iodinating agent has been shown to be a positive iodine species; (2) that deiodination is therefore a S_E2 reaction of the free amine with a solvated proton; and (3) that the rate of deiodination of the free amine depends on the H_0 acidity function, not on the concentration of hydrogen ions.

THE iodination of aromatic compounds has long been recognised as a reversible process, but recent kinetic investigations have been largely limited to the forward reaction.[1] The only detailed kinetic study of deiodination appears to be that of Gold and Whittaker [2] on the reaction of substituted phenols with hydriodic acid in aqueous acetic acid. In this medium, the kinetics of deiodination are too complex to be easily interpreted in terms of the reaction mechanism. To facilitate comparison with the kinetics of iodination, the experiments reported below were all carried out in water or deuterium oxide as solvent, and this change in medium appears greatly to simplify the kinetic form.

[1] Berliner, *J. Amer. Chem. Soc.*, 1950, **72**, 4003; cf. de la Mare and Ridd, "Aromatic Substitution," Butterworths, London, 1959, p. 120.
[2] Gold and Whittaker, *J.*, 1951, 1184.

At 100°, *p*-iodoaniline reacts at a convenient rate with dilute aqueous acids (~0·1M) containing potassium iodide (~0·5M) to give aniline and iodine, the latter as tri-iodide ions. This reaction has been followed by spectrometric and titrimetric estimation of the iodine formed. Some concurrent oxidation of iodide ions to iodine occurs in the medium. The

TABLE 1. *The dependence of the initial rate (v_0 in mole l.$^{-1}$ sec.$^{-1}$) on the concentration of* p-*iodoaniline.*

[HCl] = 0·05M. [KI] = 0·25M. Temp. 98°.

$[NH_2{\cdot}C_6H_4I]$ * (M)	0·0025	0·005	0·01	0·02
10^6v_0	17·1	34·8	65·5	134·0
10^6k_1 (sec.$^{-1}$)	68·4	69·6	65·5	67·0

* In this and the following Tables the listed amine concentration is the stoicheiometric value, not the molecular concentration of the free amine.

rate of this " blank reaction " has been studied by preparing reaction mixtures equivalent to those used in the deiodination experiments but containing no *p*-iodoaniline. Under the conditions used, the initial rate of the blank reaction was about 5—30% of that of the total reaction. Because of certain complications in comparing the blank reaction and the total reaction (see p. 826), this investigation was based on the difference in the initial rates of formation of iodine in the presence and in the absence of *p*-iodoaniline, and this value is referred to in the Tables as the initial rate of deiodination. Where the blank reaction was unimportant, rate coefficients were also calculated from integrated rate equations and an example is given on p. 826.

The variation of the initial rate of deiodination with the stoicheiometric concentration of *p*-iodoaniline is indicated in Table 1. The last line shows the values of a rate coefficient (k_1) obtained by dividing the initial rate by the concentration of *p*-iodoaniline; the constancy of k_1 indicates that the reaction is of first order with respect to the amine.

The effect of acids on the initial rate of deiodination is shown in Table 2; over the range studied the reaction rate is effectively independent of the nature and concentration of the acid. Concentrations of perchloric acid above 0·1M caused some precipitation of potassium perchlorate from the reaction mixture, and some cloudiness also appeared in the solution containing M-sulphuric acid. Experiments with these acids were therefore limited to the lower acidities.

The results in Table 3 show that the initial reaction rate is effectively independent of the concentration of potassium iodide, and no significant difference could be detected at later stages of the kinetic runs. Under the conditions of the experiments, it follows that a 0·25M-concentration of iodide ions is sufficient to displace the equilibrium in equation (1)

$$^+NH_3{\cdot}C_6H_4I + H^+ + 2I^- = {}^+NH_3{\cdot}C_6H_5 + I_3^- \quad \ldots\ldots\ldots (1)$$

in favour of almost complete deiodination. The iodide ions have no kinetic effect on the reaction rate, and so the superior efficiency of hydriodic acid over other mineral acids in aqueous deiodination appears to arise only from the mass-law effect on the above equilibrium. The results in Table 3 also show that potassium chloride has no significant effect on the reaction rate.

TABLE 2. *The dependence of the initial rate (v_0, in mole l.$^{-1}$ sec.$^{-1}$) on acidity.*

$[NH_2{\cdot}C_6H_4I]$ = 0·01M. [KI] = 0·25M. Temp. 98°.

Acid concn. (M)		0·025	0·05	0·10	0·50	1·0	2·0	4·0	6·0
10^6v_0:	HCl	71·7	65·5	71·7	65·5	70·4	70·5	67·0	79·2
	$HClO_4$	69·1	69·1	70·1	—	—	—	—	—
	H_2SO_4	—	—	—	—	67·6	—	—	—

The pK_a of *p*-iodoaniline is 3·18,[3] and so, under the conditions listed in Tables 1—3, the stoicheiometric concentration of the amine is effectively equal to the concentration of its conjugate acid. The kinetic form of the reaction is therefore as indicated in equation

[3] Bennett, Brooks, and Glasstone, *J.*, 1935, 1821.

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(2), and, in particular, the kinetic equation does not include the concentration of hydrogen ions or that of iodide ions. This result would not have been expected from other published data on deiodination [2] but it can be understood by comparing the transition states for iodination and deiodination.

$$\text{Rate} = k_1[\overset{+}{\text{N}}\text{H}_3{\cdot}\text{C}_6\text{H}_4\text{I}] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Kinetic studies on the deiodination of other aromatic compounds have shown that the reaction is an electrophilic displacement of iodine,[2] and hence, at the acid concentrations listed in Tables 1—3, almost certainly involves the free amine. The single term in equation

TABLE 3. *The dependence of the initial rate (v_0, in mole $l.^{-1}$ $sec.^{-1}$) on the concentration of potassium iodide and potassium chloride.*

$[H^+]$ * = 0·05M. $[NH_2{\cdot}C_6H_4I]$ = 0·01M. Temp. 98°.

[KI]	0·25	0·50	1·0	2·0	0·25		0·25
[KCl]	—	—	—	—	1·0		4·0
10^5v_0	65·5	60·2	70·4	69·8	71·8	73·9 †	64·6

* Set by either hydrochloric acid or perchloric acid; the difference is not kinetically significant.
† Carried out in the presence of M-hydrochloric acid.

(2) shows that the transition state contains only a free iodoaniline molecule and a proton or hydroxonium ion. The course of substitution in the free iodoaniline can therefore be written as in (3), where the possible hydration of the proton is ignored.

$$NH_2{\cdot}C_6H_4I \xrightarrow{+H^+} \left[NH_2{\cdot}C_6H_4\begin{matrix}H\\I\end{matrix}\right]^+ \xrightarrow{+2I^-} NH_2{\cdot}C_6H_5 + I_2^- \quad \ldots\ldots \quad (3)$$

The kinetic equation of the reverse reaction has been obtained from studies involving buffer solutions [1] and contains several terms, one or more arising from base-catalysis from the components of the buffer. There is also one uncatalysed term and this corresponds to a transition state containing only a free aniline molecule and an iodine cation (possibly hydrated). This is the same composition as the transition state in equation (3) and it therefore appears that the iodination and deiodination experiments involve the same reaction path, despite the considerable difference in the experimental conditions.

This similarity also extends to kinetic isotope effects. Comparison of the aqueous iodination of aniline and 2,4,6-trideuteroaniline shows a k_H/k_D ratio [4] of about 4, and the evidence from other iodinations [5] suggests that this isotope effect appears equally in the uncatalysed and the base-catalysed kinetic terms. This isotope effect must correspond to a considerable weakening of the C–H bond in the transition state, which suggests that proton loss to a water molecule is largely rate-determining. By the principle of microscopic reversibility, deiodination under the same conditions should involve a rate-determining proton transfer to *p*-iodoaniline from a hydroxonium ion. Electrophilic substitutions of this type, involving slow proton transfers from Brönsted acids, have been termed [6] $A\text{-}S_E2$.

The estimation of the corresponding isotope effect for deiodination by the same reaction path but under the conditions reported in this paper is complicated by the absence of information on the effective zero-point energy of the solvated proton. Some recent work suggests [7] that this is less than that of an aromatic proton, and so the primary isotope effect in deiodination should be less than the factor of 4 observed in iodination, and should be further reduced by the higher temperature of the deiodination runs. However, in addition, the change to a deuterated medium should decrease [8] the free amine concentration by a factor of 4 at 25° and rather less (possibly 3) at 100°. These factors, taken together, suggest that the k_{H_3O}/k_{D_3O} ratio for deiodination should be between 3 and 9.

[4] Shilov and Weinstein, *Nature*, 1958, **182**, 1300; *Doklady Akad. Nauk S.S.S.R.*, 1958, **123**, 93.
[5] Grimison and Ridd, *J.*, 1959, 3019.
[6] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.
[7] Gold, Lambert, and Satchell, *J.*, 1960, 2461.
[8] Högfeldt and Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.

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TABLE 4. *Comparison of the rate of deiodination in water and in deuterium oxide (containing 2·5% of* H_2O*).*

[HCl] = 0·05M. [$NH_2{\cdot}C_6H_4I$] = 0·01M. [KI] = 0·25M. Temp. 98°.

	$10^3[I_2]$ in H_2O			$10^3[I_2]$ in D_2O		
Time (min.)	Total	Blank	Diff.	Total	Blank	Diff.
30	1·25	0·08	1·17	0·27	0·04	0·23
60	2·39	0·12	2·27	0·56	0·09	0·48
90	3·65	0·16	3·49	0·79	0·13	0·66
120	4·52	0·23	4·29	1·03	0·19	0·84
150	5·21	0·27	4·94	1·26	0·23	1·03
180	5·93	0·32	5·61	1·52	0·28	1·24
Mean values of k_1		$76·6 \times 10^{-6}$ sec.$^{-1}$			$13·1 \times 10^{-6}$ sec.$^{-1}$	

$k_{H_2O}/k_{D_2O} = 5·8$.

Deiodinations in water and in 97·5% deuterium oxide are compared in Table 4. The conditions were adjusted so that the blank reaction was small, and rate coefficients were calculated from a logarithmic plot of the *p*-iodoaniline concentration. The ratio k_{H_2O}/k_{D_2O} is about 6. This is consistent with the expected mechanism. The conclusion that the primary isotope effect persists in dilute solutions of mineral acids is supported by a recent study [9] of the iodination of anisole, where the k_H/k_D ratio remains constant over the pH range 1—4.

This correspondence between iodination and deiodination has been stressed because it strongly reinforces the argument that deiodination, under the above conditions, occurs by an A-S_E2 mechanism, and therefore permits the kinetic data to be used as evidence of the dependence of A-S_E2 reactions on acidity. The results in Table 2 show that the overall rate of iodination remains effectively independent of acidity, even in the region where the H_0 acidity function deviates from pH. Since the concentration of the free amine is then inversely proportional to h_0 it follows that the rate of substitution in the free amine must be proportional to h_0. If the rate of this substitution were instead proportional to the concentration of the hydroxonium ions then the consideration of the product [$NH_2{\cdot}C_6H_4I$][H_3O^+] shows that, in hydrochloric acid, the overall rate of deiodination would decrease by a factor of 17 in going from [H^+] = 0·05 to [H^+] = 6·0. It is impossible to explain the discrepancy between this calculated result and the experimental data by including a large salt effect or chloride-ion catalysis since, as shown in Table 3, potassium chloride has no effect on the overall reaction rate. It seems therefore that, at least for this reaction, the rate of proton transfer from the medium * depends on the acidity function and not on the concentration of hydroxonium ions. This supports the view, recently put forward by other workers,[6,10] that criteria based on acidity functions do not distinguish between prototropic pre-equilibria (mechanism A-1) and rate-determining proton transfer (mechanism A-S_E2).

It is hoped that current studies on the deiodination of other substituted anilines will provide evidence on the factors determining the detailed mechanism of substitution.

EXPERIMENTAL

Materials.—*p*-Iodoaniline (m. p. 63°) was prepared by iodination of aniline [11] and recrystallised three times from light petroleum (b. p. 60—80°). The other components of the reaction mixtures were " AnalaR " reagents. All solids were dried before use.

Kinetic Runs.—The preliminary experiments were carried out by pipetting aliquot parts of

* One Referee has pointed out that the proton need not come from the medium since the kinetic form is consistent with an intramolecular migration of the proton from the NH_3^+ group to the *para*-position. We consider that the proton would be transferred to the solvent before such a migration could be completed.

[9] Berliner, personal communication.
[10] Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507.
[11] *Org. Synth.*, Coll. Vol. II, John Wiley and Sons, New York, 1943, p. 347.

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the reaction mixture into 50 ml. conical flasks with ground-glass stoppers secured with springs. These solutions were placed in a liquid thermostat at 98° and later withdrawn at suitable times, and the iodine was determined by titration with thiosulphate. Related experiments indicated that there was no significant catalysis by light and no loss of iodine from the stoppered flasks.

It was then found more convenient to carry out the reaction in a 1 cm. Unicam cell fitted with a B.10 stopper secured by springs. This was placed in the thermostat, removed after a suitable time, cooled at once to room temperature, cleaned, and placed in a Unicam S.P. 500 spectrophotometer. After the optical density of the solution had been measured the cell was replaced in the thermostat until the next kinetic point was required. Only the time the cell remained in the thermostat was included in the kinetic run; the rate of deiodination at room temperature is negligible. Errors associated with the time lag of heating to the thermostat temperature were partly compensated by the continuance of reaction during cooling; comparison with the method used for the preliminary experiments indicated that the intermittent heating did not cause appreciable error.

The measurements of optical density were carried out at 500 mμ with a slit width of 0·035 mm. Under the experimental conditions the only effective light absorption at this wavelength is by the I_3^- ion, and the optical density is therefore proportional to the analytical concentration of iodine. The optical density is not significantly affected by other solutes present over the range of components and concentrations listed in Tables 1—4. The extinction coefficient of the I_3^- ion under the above conditions is $2{\cdot}63 \times 10^2$.

Calculation of the Rate of Deiodination.—Each kinetic experiment on deiodination was accompanied by an equivalent kinetic run carried out in the absence of *p*-iodoaniline but corrected where necessary to the same effective hydrogen-ion concentration. The difference between the iodine content of the solutions was attributed to deiodination. The implicit assumption that *p*-iodoaniline does not catalyse or anti-catalyse the oxidation of iodide ions to iodine is supported by the fact that the net rate of formation of iodine is independent of the concentration of iodide ions (see eqn. 2). Also, in a single kinetic run, the net rate of iodine formation is of first order with respect to the concentration of *p*-iodoaniline, when the latter is calculated on the assumption that the net iodine formed comes only from deiodination. This is illustrated by the integrated rate coefficients below, calculated for the first kinetic run listed in Table 4, where the blank reaction is not important:

Time (min.)	0	30	60	90	120	150	180
$10^3[NH_2{\cdot}C_6H_4I]$ (mole $l.^{-1}$)	10	8·83	7·73	6·51	5·71	5·06	4·39
$10^5 k_1$ ($sec.^{-1}$)	—	6·9	7·8	8·0	7·8	7·6	7·6

Since the deiodination uses up hydrogen ions, the reaction mixture and the blank solution are truly equivalent only at the start of the kinetic run, and this factor introduces considerable error into the calculation of integrated rate coefficients for some of the kinetic runs. For consistency, the results in Tables 1—3 are all quoted in terms of the initial rate of deiodination. These values in fact refer to the mean rate of deiodination over the first 10% of reaction and are therefore a little lower than the true initial rate; they are also subject to experimental errors of about ±5%. The accuracy of these results is therefore a little less than that usually reported, but more than sufficient for the mechanistic distinctions referred to above.

Analysis of Products.—A solution of *p*-iodoaniline (0·01 mole) in 0·05M-perchloric acid (1 l.) containing 0·5M-potassium iodide was heated to 98° for 12 hr., cooled, decolorised with sodium hydrogen sulphite, made alkaline with sodium hydroxide, and then extracted with ether. The ether layer was separated, and the ether distilled off. The remaining oil was treated with bromine water to give a 90% yield of crude 2,4,6-tribromoaniline (m. p. and mixed m. p. 121° after recrystallisation from 50% ethanol). A sample mixed with 2,6-dibromo-4-iodoaniline melted gradually, over the range 110—140°.

The authors thank Sir Christopher Ingold, F.R.S., and Professor E. D. Hughes, F.R.S., for their interest in the work. One of them (H. S. C.) thanks the National Science Foundation, U.S.A., for Science Teacher Fellowship which made this work possible.

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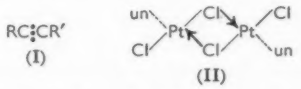
176. *Complexes of Acetylenes with Platinum*(II). *Part I. Alkynes.*

By J. Chatt, R. G. Guy, and (in part) L. A. Duncanson.

Alkyne–platinum(II) complexes of the chloro-bridged type $[Pt_2Cl_4ac_2]$ and the mononuclear type $M[PtCl_3ac]$ (M = Na or K, ac = alkyne) are described. The simplest alkynes which have formed stable complexes are of the type $Bu^tC{\equiv}CR$ (R = Bu^t, Pr^i, Et, Me, or CMe_2Ph). Amines (am) react with the complexes to give mononuclear complexes of the type *trans*-$[PtCl_3ac\ am]$.

The infrared spectra of the complexes show that in the complex the frequency of the stretching vibration of the C≡C bond is lowered by some 200 cm.$^{-1}$. This is consistent with a structure similar to that of the corresponding olefin complexes. The dipole moments of complexes of the type *trans*-$[PtCl_2un\ am]$ (un = $Bu^tC{\equiv}CBu^t$ or C_2H_4) show that the $Bu^tC{\equiv}CBu^t \longrightarrow$ Pt group moment is about 1·0 D greater than the $C_2H_4 \longrightarrow$ Pt group moment.

Stable platinum(II) complexes containing olefins as ligands have been known since 1827 when Zeise [1] reported the ethylene complex $K[PtCl_3(C_2H_4)],H_2O$. Since then many olefin complexes of platinum(II) have been described,[2,3] but attempts to prepare the corresponding platinum(II) complexes of acetylene and monosubstituted alkynes led to indefinite, reddish-brown amorphous products, owing probably to replacement of the ethynyl hydrogen atoms. The first stable acetylene complex was reported by Gel'man *et al.*,[4] who showed that the acetylenic glycol $HO{\cdot}CMe_2{\cdot}C{\equiv}C{\cdot}CMe_2{\cdot}OH$ (ac) forms a complex, *trans*-$[PtCl_2ac\ py]$, analogous to *trans*-$[PtCl_2(C_2H_4)\ py]$ (py = pyridine). Later work [5,6,7] showed that this glycol further resembles olefins in forming complexes of the types $K[PtCl_3ac]$ and *cis*-$[PtCl_2ac\ NH_3]$ by the common methods used to prepare the corresponding olefin complexes. Chatt and Duncanson [8] were nevertheless unable to prepare the corresponding complexes of dimethylacetylene and diphenylacetylene by any of these methods, although colour changes were observed which suggested that some unstable complex was formed.



(I) (II)

In an attempt to find the reason for this difference between the stabilities of complexes derived from the acetylenic glycol and the acetylenic hydrocarbons $MeC{\equiv}CMe$ and $PhC{\equiv}CPh$ we have examined the reactions of a series of acetylenic hydrocarbons and alcohols with (*a*) aqueous potassium tetrachloroplatinate(II), (*b*) ethanolic sodium tetrachloroplatinate(II), (*c*) $K[PtCl_3(C_2H_4)]$ in acetone, and (*d*) $[Pt_2Cl_4(C_2H_4)_2]$ in acetone. We have also examined the infrared spectra of all the complexes which we have obtained from these reactions, with particular reference to the effect of complex formation on the O–H stretching frequencies and bands which we assign, but with rather less certainty, to the C≡C stretching frequencies.

In this paper we describe the preparation of complexes derived from alkynes of the type (I) and show (i) that the stability depends greatly on the groups R, and (ii) that the complexes are exactly analogous to the olefin complexes.[9] The complexes of acetylenic

[1] Zeise, *Pogg. Annalen*, 1827, **9**, 632.
[2] See Keller, *Chem. Rev.*, 1941, **28**, 229.
[3] See Douglas, "The Chemistry of the Co-ordination Compounds," ed. Bailar, Reinhold Publ. Inc., New York, 1956, p. 487.
[4] Gel'man, Bukhovets, and Meilakh, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **46**, 105.
[5] Bukhovets, *Izvest. Sekt. Platiny drug. blagorod. Metal., Inst. obschchei neorg. Khim.*, 1955, **29**, 55.
[6] Bukhovets and Molodova, *Zhur. neorg. Khim.*, 1957, **2**, 776; 1958, **3**, 1540.
[7] Molodova, *Zhur. neorg. Khim.*, 1958, **3**, 2472.
[8] Chatt and Duncanson, *J.*, 1953, 2939.
[9] For a preliminary account of this work, see Chatt, Duncanson, and Guy, *Chem. and Ind.*, 1959, 430.

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alcohols and platinum(II) show special features which are discussed elsewhere,[10] and will be described in detail in Part II.

To see whether the hydroxyl groups in the glycol $HO{\cdot}CMe_2{\cdot}C{\equiv}C{\cdot}CMe_2{\cdot}OH$ are essential for the formation of stable complexes, the related alkyne 2,2,5,5-tetramethylhex-3-yne (I; R = R′ = Bu^t) was first investigated. When an ethanolic solution of sodium chloroplatinate(II) tetrahydrate is treated at room temperature for several days with an excess of 2,2,5,5-tetramethylhex-3-yne ($C_{10}H_{18}$), a red, crystalline solid of composition $C_{10}H_{18}Cl_2Pt$ is formed in 81% yield (method 1). This compound can also be obtained more readily in 74% yield by reaction of the alkyne with ethyleneplatinous chloride (II; un = C_2H_4) in acetone (method 2).

$$2Na_2PtCl_4 + 2C_{10}H_{18} \longrightarrow [Pt_2Cl_4(C_{10}H_{18})_2] + 4NaCl \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$[Pt_2Cl_4(C_2H_4)_2] + 2C_{10}H_{18} \longrightarrow [Pt_2Cl_4(C_{10}H_{18})_2] + 2C_2H_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The complex, $C_{10}H_{18}Cl_2Pt$, is dimeric, diamagnetic, and a non-electrolyte in nitrobenzene. It is moderately soluble in light petroleum, very soluble in other common organic solvents, and insoluble in water. It is stable, even on exposure to the atmosphere, in contrast to ethyleneplatinous chloride. It melts at 184—187° with decomposition, and sublimes poorly, with extensive decomposition, at 150°/0·01 mm.

It has the bridged structure (II; un = Bu^{t}C≡CBu^t) analogous to that of ethyleneplatinous chloride (II; un = C_2H_4). The existence of the halogen bridge was confirmed by bridge-splitting reactions with amines (am) to give mononuclear complexes, and with potassium chloride to give the analogue of Zeise's salt, $K[PtCl_3(C_{10}H_{18})]$, *i.e.*:

$$[Pt_2Cl_4(C_{10}H_{18})_2] + 2am \longrightarrow 2\textit{trans}\text{-}[PtCl_2(C_{10}H_{18})\,am]$$

$$[Pt_2Cl_4(C_{10}H_{18})_2] + 2KCl \longrightarrow 2K[PtCl_3(C_{10}H_{18})]$$

The amine derivatives prepared (am = pyridine, 4-chloropyridine, 4-methylpyridine, piperidine, and *p*-toluidine) are stable, yellow, crystalline solids, readily soluble in all the common organic solvents except light petroleum. The ionic complex, $K[PtCl_3(C_{10}H_{18})]$, is stable in the dry state, but on addition of water it instantly reverts to the bridged complex.

This ionic complex can also be prepared by direct replacement of the ethylene in $K[PtCl_3(C_2H_4)],H_2O$ by the alkyne (method 3). At room temperature displacement of the ethylene is incomplete after 8 days, but in boiling acetone the reaction goes to completion in 3 hours.

$$K[PtCl_3(C_2H_4)],H_2O + C_{10}H_{18} \longrightarrow K[PtCl_3(C_{10}H_{18})] + C_2H_4 + H_2O \quad . \quad . \quad . \quad . \quad (3)$$

The bromo-bridged complex corresponding to (II; un = Bu^{t}C≡CBu^t) is formed in 26% yield by treatment of potassium bromoplatinate(II) with 2,2,5,5-tetramethylhex-3-yne in aqueous acetone. This deep-red complex is analogous in every way to the chloro-complex, and is equally stable.

The alkynes Bu^{t}C≡CR (R = Pr^i, Et, CMe_2Ph) readily yield the bridged complexes (II; un = Bu^{t}C≡CPr^i, Bu^{t}C≡CEt, and Bu^{t}C≡C·CMe_2Ph respectively) by both methods 1 and 2. These complexes are stable, and undergo the normal bridge-splitting reactions with amines to give stable complexes of the type *trans*-$[PtCl_2(Bu^tC{\equiv}CR)(amine)]$. 2,2-Dimethylpent-3-yne (Bu^{t}C≡CMe), however, gives the ionic complex $Na[PtCl_3(Bu^tC{\equiv}CMe)]$ on treatment with ethanolic $Na_2PtCl_4,4H_2O$ (method 1). Aqueous solutions of this complex, in contrast to $K[PtCl_3(Bu^tC{\equiv}CBu^t)]$, are stable, and react with amines in the manner of Zeise's salt to give complexes of the type *trans*-$[PtCl_2(Bu^tC{\equiv}CMe)(amine)]$. Reaction of Bu^{t}C≡CMe with ethyleneplatinous chloride (method 2) did not yield the binuclear complex (II; un = Bu^{t}C≡CMe), which was not obtained even by the reaction of an alcoholic solution of hydrogen chloride on the salt $K[PtCl_3(Bu^tC{\equiv}CMe)]$.

The alkynes Bu^{t}C≡CH, Pr^{i}C≡CH, Pr^{i}C≡CEt, Pr^{i}C≡CMe, Bu^{n}C≡CBu^n, Pr^{n}C≡CPr^n, EtC≡CEt,

[10] Chatt, Duncanson, and Guy, *Nature*, 1959, **184**, 526.

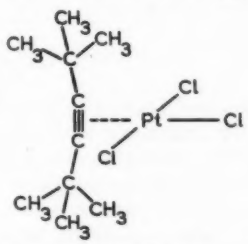
MeC:CMe, PhC:CPh, Bu^t·[C:C]$_2$·Bu^t, and Ph·[C:C]$_2$·Ph showed colour changes indicative of complex formation when treated by methods 1, 2, and 3. In some cases extensive decomposition products were rapidly formed, and in all cases the products were too unstable to be isolated by rapid evaporation of their solutions at water-pump pressure and below 10°. Attempts to form complexes of the type *trans*-[$PtCl_2$ac am] (ac = alkyne, am = amine) by addition of the appropriate amount of amine to the reaction solution were equally unsuccessful. In general, these alkynes gave intractable brown or black gums when treated by methods 1 and 2, and yellow-brown solids, insoluble in water and of variable composition, when treated by method 3.

Hydration of the triple bond of the alkyne, presumably catalysed by colloidal platinum formed by reduction of the platinum(II) salt, occurred in the reaction of several alkynes with ethanolic $Na_2PtCl_4,4H_2O$; *e.g.*, Bu^nC:CBu^n gave decan-5-one, and PhC:CPh gave benzyl phenyl ketone.

Infrared Spectra (In collaboration with L. A. Duncanson).—The C:C stretching frequency in disubstituted alkynes [11] occurs between 2190 and 2260 cm.$^{-1}$, the intensity of absorption in the infrared region depending on the asymmetry of the alkyne. If the alkynes are bound to the platinum atom in the same manner as olefins, we should find weak absorption bands in the infrared spectra of the complexes corresponding to the C:C stretching frequencies, especially when the alkyne is not symmetrical about the triple bond. We have therefore examined the infrared spectra of the powdered crystalline complexes.

The symmetrical complex (II; un = Bu^tC:CBu^t) has two weak absorption bands at 2023 and 2005 cm.$^{-1}$, and all the other complexes show a single weak absorption band between 2001 and 2028 cm.$^{-1}$ (see Table 1). This absorption band does not correspond to any known C–C absorption, and as it occurs in the spectrum of all types of complexes

Probable spatial arrangement of atoms in [$PtCl_3(Bu^t$C:C$Bu^t]^-$.



of alkynes and hydroxyacetylenes with platinum(II),[10] it is attributed to the C:C stretching frequency, lowered by some 200 cm.$^{-1}$ by co-ordination to the platinum atom. This lowering of frequency may be compared with (*a*) the lowering of 140 cm.$^{-1}$ in the C:C stretching frequency of olefins on complex formation with platinum(II),[8] (*b*) the lowering of 400 cm.$^{-1}$ in the C:C stretching frequency of acetylenes on complex formation with platinum(0),[12] and (*c*) the lowering of 65 cm.$^{-1}$ in the C:C stretching frequency of olefins on complex formation with silver(I).[13]

The existence of the weak absorption near 2000 cm.$^{-1}$ in the complex (II; un = Bu^tC:CBu^t) is evidence of the loss of a centre of symmetry by the alkyne, but, as with ethylene, its weakness indicates that the symmetry of the alkyne has not been altered by co-ordination to the metal. The alkyne thus appears to be symmetrically co-ordinated about the triple bond, in exactly the same manner as the olefins, and bound to the metal by the same type of double bond as ethylene in Zeise's salt.[8] The σ-component of the bond would be formed by overlap of a $5d6s6p^2$-hybrid orbital of the platinum atom with a π-orbital of the alkyne, and the π-type bond by overlap of a filled $5d6p$-orbital with an antibonding π-molecular orbital of the alkyne. This should lead to the spatial arrangement

[11] See Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 59.
[12] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.
[13] Taufen, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3500.

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of atoms in $[PtCl_3(Bu^tC{:}CBu^t)]^-$ shown in the Figure. Since the symmetrical distribution of electron density about the C:C axis of the alkyne will be disturbed in the complex it seems probable that the alkyne will also be slightly bent as shown.

The effect of the alkyne on the electronic distribution in the Pt–N bond of *trans*-[$PtCl_2$ac piperidine] was investigated by measuring the N–H stretching frequency (ν_{N-H}) of the complexes in dilute carbon tetrachloride solution.[14] It can be seen from Table 1 that ν_{N-H} in these complexes is remarkably constant, and appears to be independent of the nature of the group R in $Bu^tC{:}CR$. It is also very close to the value of 3230 cm.$^{-1}$ obtained for ν_{N-H} in *trans*-[$PtCl_2(C_2H_4)$piperidine],[14] again indicating that the alkyne must be bonded in essentially the same way as ethylene.

Dipole Moments.—The bond between the alkyne and the metal atom is a combination of two electronic effects, *i.e.*, the σ-bond, involving sharing of the π-electrons of the alkyne, and the π-bond, involving sharing of the 5*d*-electrons of the metal. To determine the polarity of the alkyne–platinum(II) bond we have measured the dipole moments of the complexes *trans*-[$PtCl_2(Bu^tC{:}CBu^t)$am] (where am = pyridine, 4-methylpyridine, and 4-chloropyridine).

The results (Table 3) show conclusively that the amine molecule is at the positive end of the permanent dipole, and thus appears to be a stronger electron-donor than the alkyne. The moment of the Pt–N bond is unknown, but is perhaps of the order 6 D, so that the

TABLE 1. *Complexes of alkynes with platinum*(II).

Alkyne (ac)	$\nu_{C:C}$ (cm.$^{-1}$) Na[$PtCl_3$ac]	$[Pt_2Cl_4ac_2]$	ν_{N-H} (cm.$^{-1}$) *trans*-[$PtCl_2$ac pip] *
$Bu^tC{:}CBu^t$	—	2023, 2005	3221
$Bu^tC{:}CPr^i$	—	2011	3221
$Bu^tC{:}CEt$	—	2023	3222
$Bu^tC{:}CMe$	2028	—	3221
$Bu^tC{:}C{\cdot}CMe_2Ph$	—	2001	3222

* pip = piperidine.

moment of the alkyne–Pt entity has a value of about 3·25 D. This is 1·0 D greater than the ethylene–Pt entity which we have remeasured more accurately than previously.[8] A greater electron drift from the alkyne to the metal atom is to be expected because the alkyne has a lower ionisation potential than ethylene (Table 2), but at this point it is not possible to say whether the increase of 1·0 D is due entirely to this effect, or whether a substantial part is due to bending of the alkyne molecule in the complex so that the positively charged t-butyl group moves away from the platinum atom as shown in the Figure.

Effect of the Structure of the Alkyne on Complex Formation.—The stabilities of the complexes depend greatly upon the structures of the alkynes they contain. Of the alkynes studied, only those containing at least one t-butyl group adjacent to the triple bond *e.g.*, $Bu^tC{:}CR$ (R = Bu^t, Pr^i, Et, Me, or CMe_2Ph), formed complexes sufficiently stable to

TABLE 2. *Ionisation potentials of alkynes.**

Alkyne	EtC:CEt	$Pr^nC{:}CPr^n$	$Bu^nC{:}CBu^n$	$Bu^tC{:}CBu^t$	$Bu^tC{:}CEt$
Ionisation potential (±0·03 ev)	9·33	9·19	9·14	9·07	9·20

* Ethylene has an ionisation potential of 10·45 ev.[16]

be isolated by the methods we used. The simpler alkynes, *e.g.*, $Bu^tC{:}CH$, $Pr^iC{:}CEt$, and RC:CR (R = Me, Et, Pr^n, or Bu^n), and alkynes conjugated to phenyl groups or another triple bond, *e.g.*, PhC:CPh and $Bu^t{\cdot}[C{:}C]_2{\cdot}Bu^t$ do not form sufficiently stable complexes. There appears to be a similar, although not so marked, dependence of the stabilities of olefin complexes upon the structures of the olefins; both methyl- and phenyl-ethylenes form complexes with platinum(II), and the former are more stable than the latter.[15] The

[14] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.
[15] Anderson, *J.*, 1936, 1042; Joy and Orchin, *J. Amer. Chem. Soc.*, 1959, **81**, 310.

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dipole moments reported in this paper show that the olefinic and acetylenic hydrocarbons in their complexes with platinum(II) behave essentially as electron donors and acquire a small positive charge in the complex. It seems logical therefore to suppose that the electron-donating methyl groups would assist, and the electronegative phenyl groups diminish, the tendency to complex formation, but such inductive effects are not sufficient to explain the enormous differences between the stabilities of the alkyne complexes.

The first ionisation potential is a measure of the donor capacity of the alkyne and in Table 2 we list a representative selection of potentials,[16] kindly measured for us by W. C. Price, P. V. Harris, and R. Bralsford. It will be seen that there is no direct correlation between the ionisation potential of an alkyne and its tendency to form stable complexes. Thus di-n-butylacetylene (dec-5-yne) appears to have a greater electron-donor capacity than ethyl-t-butylacetylene (oct-3-yne), but only the latter forms stable complexes.

Other factors which could affect the stabilities of the complexes are: (*a*) the polarisabilities of the groups adjacent to the triple bond, (*b*) the ease with which the alkyne is destroyed, *e.g.*, by isomerisation into an allene,† (*c*) the steric effects of the groups adjacent to the triple bond.

The polarisabilities of the Me, Et, Pr^i, and Bu^t groups are 27, 47, 65, and 84 $\times$ 10^{-25} cm.^{3} respectively,[17] and the high polarisability of the t-butyl group might be expected to assist the electron release from the triple bond to the platinum atom. However, if this were so, we would expect this electron release to affect the NH stretching frequency (ν_{N-H}) in the complexes of the type *trans*-[$PtCl_2(Bu^tC{:}CR)$ (piperidine)], but ν_{N-H} is independent of the group R. Also the total polarisability of the groups adjacent to the triple bond in the alkyne $Bu^tC{:}CMe$ is almost exactly equal to the polarisability of those in $Pr^iC{:}CEt$, yet the former forms complexes and the latter does not. It seems therefore that the polarisability of the groups is not an important factor.

We do not know how the unstable alkyne complexes decompose. The decomposition may involve some attack on the alkyne itself, or upon the platinum atom. If the decomposition involves some rearrangement of the alkyne, perhaps to form an allene, then those alkynes with a t-butyl group adjacent to the triple bond would rearrange less readily and should form the more stable complexes, as is found. Some factor of this type may be responsible for the greater stability of the alkyne complexes which contain t-butyl groups adjacent to the triple bond.

The steric effect of the t-butyl group could also be important. It has been shown that in complex compounds of the type *trans*-[$MClPh(PR_3)_2$](M = Ni,Pt) an *ortho*-substituent in the phenyl group has a very marked stabilising effect,[18] and one result is undoubtedly that it screens the metal atom from attack by solvent or reagent. Even one *ortho*-substituent has so great an effect that it seems possible that the t-butyl group of the alkynes could function in an analogous manner and stabilise the complex.

It should be possible to isolate some of the less stable alkyne complexes as anions by the use of large cations. We have not done this but Bukhovets and Pukhova[19] have recently isolated the complex $Et_3NH[PtCl_3(PhC{:}CPh)]$ from the reaction of $[Et_3NH]_2[PtCl_4]$ with diphenylacetylene in chloroform. The large cation with its relatively low polarising power evidently forms a stable salt with the diphenylacetylene complex ion.

Experimental

The microanalyses were carried out in these laboratories. M. p.s were determined on a Kofler hot-stage and are corrected. Except where otherwise stated, light petroleum had b. p. 60—80°.

† We are indebted to Dr. B. L. Shaw for this suggestion.

[16] Cf. Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207.
[17] Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3229.
[18] Chatt and Shaw, *J.*, 1959, 4020; 1960, 1718.
[19] Bukhovets and Pukhova, *Zhur. neorg. Khim.*, 1958, **3**, 1714.

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Preparation of Alkynes.—The alkynes, prepared as below, were purified by fractional distillation or recrystallisation immediately before use.

But-2-yne was prepared from ethyl methyl ketone by the general method of Bartlett and Rosen,[20] and had b. p. 27°/752 mm., n_D^{17} 1·3912. Similarly prepared were 3-methylbut-1-yne (b. p. 26·5—27·5°/756 mm., n_D^{20} 1·3758) from isopropyl methyl ketone, and 3,3-dimethylbut-1-yne (b. p. 37·5—38°/760 mm., n_D^{20} 1·3730) from methyl t-butyl ketone. Hex-3-yne (b. p. 81·5—82°/763 mm., n_D^{25} 1·4090), oct-4-yne (b. p. 130°/758 mm., n_D^{20} 1·4238), and dec-5-yne (b. p. 114°/100 mm., n_D^{25} 1·4318) were prepared by Bried and Hennion's method.[21] 2-Methylpent-3-yne was prepared by the alkylation of 3-methylbut-1-yne with methyl iodide in liquid ammonia, and had b. p. 72·5°/751 mm., n_D^{25} 1·4034. Similarly prepared were 2-methylhex-3-yne (b. p. 94—94·5°/749 mm., n_D^{22} 1·4090) from 3-methylbut-1-yne and ethyl bromide, 2,2-dimethylpent-3-yne (b. p. 82—82·5°/745 mm., n_D^{25} 1·4058) from 3,3-dimethylbut-1-yne and methyl iodide, and 2,2-dimethylhex-3-yne (b. p. 102°/760 mm., n_D^{25} 1·4082) from 3,3-dimethylbut-1-yne and ethyl bromide. 2,2,5-Trimethylhex-3-yne [22] had b. p. 109—110°/753 mm., n_D^{25} 1·4086, and 2,2,5,5-tetramethylhex-3-yne [23] had b. p. 110°/757 mm., n_D^{15} 1·4090. 2,2,7,7-Tetramethylocta-3,5-diyne (m. p. 130—130·5°) was prepared by aerial oxidation of a solution of 3,3-dimethylbut-1-yne and cuprous chloride in ethanolic ammonia. 1,4-Diphenylbut-1,3-diyne (m. p. 87—88°) was similarly prepared from phenylacetylene.

2,2,5-*Trimethyl-5-phenylhex-3-yne*. 2-Chloro-2,5,5-trimethylhex-3-yne [23] (15·8 g., 0·1 mole) in ether (100 ml.) was added dropwise to a stirred, ice-cold solution of phenylmagnesium bromide (0·2 mole) in ether (100 ml.). The mixture was stirred overnight at room temperature, and then heated under reflux for 2 hr. Hydrolysis at *ca.* −10° with dilute hydrochloric acid and isolation of the product from the ethereal layer gave 2,2,5-*trimethyl-5-phenylhex-3-yne* (6·75 g., 34%), b. p. 103—104°/12 mm., n_D^{25} 1·4890 [Found: C, 90·2; H, 9·95; microhydrogenation (Pd–AcOH), 1·95H_2. $C_{15}H_{20}$ requires C, 89·95; H, 10·05%; 2H_2].

Preparation of Complexes.—(1) *Complexes of the type* [$Pt_2Cl_4ac_2$]. Method 1. Sodium chloroplatinate(II) tetrahydrate (0·01 mole) in ethanol (40 ml.) was treated with the alkyne (0·02 mole) at room temperature. In 3—5 days the solution became orange-yellow and deposition of sodium chloride ceased. Ethanol was removed from the filtered solution at 15 mm. (water-bath temperature 30°). The solid residue was treated with ether, and unchanged sodium chloroplatinate(II) was filtered off. Evaporation of the solvent at 15 mm. and recrystallisation of the resulting solid from light petroleum gave the complexes described below.

Method 2. Di-μ-chlorodichlorodi(ethylene)diplatinum(II), [$Pt_2Cl_4(C_2H_4)_2$] (0·001 mole), in acetone (20 ml.) at −70° was treated with a solution of the alkyne (0·003 mole) in acetone (10 ml.). On spontaneous warming, the solution gradually became orange-red. After 2 hr. at room temperature, the solvent was removed at 15 mm., leaving the solid complex which was recrystallised from light petroleum.

The following compounds have been prepared by each of the above methods. The yields quoted are those obtained by methods 1 and 2 respectively. *Di-μ-chlorodichlorodi-*(2,2,5,5-*tetramethylhex-3-yne*)*diplatinum*(II), [$Pt_2Cl_4(Bu^tC{:}CBu^t)_2$], red prisms, m. p. 184—187° (decomp.) yields 81 and 74% (Found: C, 29·85; H, 4·55%; *M*, ebullioscopically in 0·904% benzene solution, 785. $C_{20}H_{36}Cl_4Pt_2$ requires C, 29·7; H, 4·5%; *M*, 808); *di-μ-chlorodichlorodi-*(2,2,5-*trimethylhex-3-yne*)*diplatinum*(II), [$Pt_2Cl_4(Bu^tC{:}CPr^i)_2$], red prisms, m. p. 110—114° (decomp.), yields 52 and 78% (Found: C, 27·8; H, 4·25%; *M*, cryoscopically in 1·257% benzene solution, 838. $C_{18}H_{32}Cl_4Pt_2$ requires C, 27·7; H, 4·15%; *M*, 780); *di-μ-chlorodichlorodi-*(2,2-*dimethylhex-3-yne*)*diplatinum*(II), [$Pt_2Cl_4(Bu^tC{:}CEt)_2$], orange-red prisms, m. p. 95—98·5° (decomp.), yields 91 and 76% (Found: C, 25·5; H, 3·85%; *M*, ebullioscopically in 0·434% benzene solution, 736. $C_{16}H_{28}Cl_4Pt_2$ requires C, 25·55; H, 3·75%; *M*, 752); *di-μ-chlorodichlorodi-*(2-*phenyl*-2,5,5-*trimethylhex-3-yne*)*diplatinum*(II), [$Pt_2Cl_4(Bu^tC{:}C{\cdot}CMe_2Ph)_2$], red prisms, m. p. 158—161° (decomp.), yields 73 and 60% (Found: C, 38·8; H, 4·35%; *M*, ebullioscopically in 0·833% benzene solution, 978. $C_{30}H_{40}Cl_4Pt_2$ requires C, 38·65; H, 4·3%; *M*, 933).

Di-μ-bromodibromodi-(2,2,5,5-tetramethylhex-3-yne)diplatinum(II), [$Pt_2Br_4(Bu^tC{:}CBu^t)_2$]. Potassium tetrabromoplatinate(II) (0·01 mole) in water (50 ml.) was treated with 2,2,5,5-tetramethylhex-3-yne (0·011 mole) in acetone (20 ml.) at room temperature. After 8 days the

[20] Bartlett and Rosen, *J. Amer. Chem. Soc.*, 1942, **64**, 543.
[21] Bried and Hennion, *J. Amer. Chem. Soc.*, 1937, **59**, 1310.
[22] Helmkamp, Carter, and Lucas, *J. Amer. Chem. Soc.*, 1957, **79**, 1306.
[23] Hennion and Banigan, *J. Amer. Chem. Soc.*, 1946, **68**, 1202.

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red-brown solid which had formed was collected and recrystallised from light petroleum. This afforded the *complex* as dark red prisms, m. p. 189—193° (decomp.), in 26% yield (Found: C, 24·2; H, 3·65%; *M*, ebullioscopically in 0·645% benzene solution, 1034. $C_{20}H_{36}Br_4Pt_2$ requires C, 24·35; H, 3·7%; *M*, 986). No complex of the type K[$PtBr_3$ac] was detected in the aqueous mother-liquors.

(2) *Complexes of the type* M[$PtCl_3$ac]. (*a*) Potassium trichloro-(2,2,5,5-tetramethylhex-3-yne)platinate(II), K[$PtCl_3$($Bu^tC{:}CBu^t$)]. Preparation 1. A solution of Zeise's salt (1 mol.) and 2,2,5,5-tetramethylhex-3-yne (2 mol.) in acetone (25 ml.) was heated under reflux for 3 hr. The cooled solution was filtered from a small amount of colloidal platinum and taken to dryness at 15 mm., yielding the *complex* as yellow prisms, decomp. 210—220°, in 89% yield (Found: C, 24·7; H, 3·8. $C_{10}H_{15}Cl_3KPt$ requires C, 25·1; H, 3·8%).

Preparation 2. Di-μ-chlorodichlorodi-(2,2,5,5-tetramethylhex-3-yne)diplatinum(II) (0·0005 mole) in acetone (5 ml.) was treated with a solution of potassium chloride (0·001 mole) in water (5 ml.). Reaction was immediate and was accompanied by a colour change from orange-red to yellow. The solution was taken to dryness at 15 mm., the solid residue treated with acetone, and solvent removed at 15 mm. from the filtered solution. The residue, after being washed with ether, yielded the complex as a pale yellow solid, decomp. 210—220°, in quantitative yield (Found: C, 24·7; H, 3·8%).

(*b*) Sodium trichloro-(2,2-dimethylpent-3-yne)platinate(II), Na[$PtCl_3$($Bu^tC{:}CMe$)]. Sodium chloroplatinate(II) was treated with 2,2-dimethylpent-3-yne as described for method 1. The yellow solid obtained on evaporation of the ethanol was treated with acetone, and the filtered solution taken to dryness at 15 mm. The residue was washed with ether, yielding the *complex* as yellow prisms, decomp. 200—210°, in 43% yield (Found: C, 19·55; H, 2·9. $C_7H_{12}Cl_3NaPt$ requires C, 20·0; H, 2·9%).

(3) *Complexes of the type* trans-[$PtCl_2$ac am]. *General method.* The dinuclear complex [$Pt_2Cl_4ac_2$] (0·001 mole) in acetone (5 ml.) was treated with a solution of the amine (0·002 mole) in acetone (5 ml.) at room temperature. The reaction was immediate, and was accompanied by a change in colour from orange-red to yellow. The solution was then taken to dryness at 15 mm. in the cold, and the residue recrystallised.

Prepared in this way were: trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(p-*toluidine*)-*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CBu^t$)(*p*-$Me{\cdot}C_6H_4{\cdot}NH_2$)], yellow prisms from benzene–light petroleum, m. p. 189—193° (decomp.), 70% yield (Found: C, 39·75; H, 5·35; N, 3·0. $C_{17}H_{27}Cl_2NPt$ requires C, 39·9; H, 5·3; N, 2·75%); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(*piperidine*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CBu^t$)($C_5H_{11}N$)], yellow needles (from light petroleum), m. p. 154—157° (decomp.) 55% yield (Found: C, 37·05; H, 6·2; N, 3·05. $C_{15}H_{29}Cl_2NPt$ requires C, 36·8; H, 6·0; N, 2·85%); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)-(*pyridine*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CBu^t$)(C_5H_5N)], dark yellow prisms (from light petroleum), m. p. 152—156° (decomp.), 66% yield (Found: C, 37·2; H, 4·85; N, 3·0%; *M*, ebullioscopically in 0·849% benzene solution, 461; in 1·062% benzene solution, 450. $C_{15}H_{23}Cl_2NPt$ requires C, 37·25; H, 4·8; N, 2·9%; *M*, 483); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(γ-*picoline*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CBu^t$)(4-$Me{\cdot}C_5H_4N$)], yellow prisms (from benzene–light petroleum), m. p. 154—159° (decomp.), 54% yield (Found: C, 38·75; H, 5·3; N, 3·0. $C_{16}H_{25}Cl_2NPt$ requires C, 38·65; H, 5·05; N, 2·8%); trans-*dichloro*-(2,2,5,5-*tetramethylhex*-3-*yne*)(4-*chloropyridine*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CBu^t$)(4-$Cl{\cdot}C_5H_4N$)], yellow prisms (from benzene–light petroleum), m. p. 160—165° (decomp.), 57% yield (Found: C, 34·85; H, 4·4; N, 3·0. $C_{15}H_{23}Cl_2NPt$ requires C, 34·8; H, 4·3; N, 2·7%); trans-*dichloro*-(2,2,5-*trimethylhex*-3-*yne*)(*piperidine*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CPr^i$)($C_5H_{11}N$)], bright yellow prisms [from light petroleum (b. p. 40—60°)], m. p. 60—65° (decomp.), 51% yield (Found: C, 34·95; H, 5·7; N, 3·0. $C_{14}H_{27}Cl_2NPt$ requires C, 35·5; H, 5·7; N, 2·95%); trans-*dichloro*-(2,2-*dimethylhex*-3-*yne*)-(*piperidine*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}CEt$)($C_5H_{11}N$)], yellow prisms (from light petroleum), m. p. 55—58·5° (decomp.), 38% yield (Found: C, 33·8; H, 5·55; N, 3·15. $C_{13}H_{25}Cl_2NPt$ requires C, 33·85; H, 5·45; N, 3·05%); trans-*dichloro*-2,2,5-*trimethyl*-5-*phenylhex*-3-*yne*)-(*piperidine*)*platinum*(II), *trans*-[$PtCl_2$($Bu^tC{:}C{\cdot}CMe_2Ph$)($C_5H_{11}N$)], yellow prisms (from light petroleum), m. p. 96·5—100° (decomp.), 64% yield (Found: C, 43·4; H, 6·0; N, 2·55. $C_{20}H_{31}Cl_2NPt$ requires C, 43·55; H, 5·65; N, 2·55%).

trans-Dichloro-(2,2-dimethylpent-3-yne)(piperidine)platinum(II), *trans*-[$PtCl_2$($Bu^tC{:}CMe$)($C_5H_{11}N$)]. Sodium trichloro-(2,2-dimethylpent-3-yne)platinate(II), Na[$PtCl_3$($Bu^tC{:}CMe$)] (0·002 mole), in water (7 ml.) was treated at 0° with piperidine (0·002

mole), yielding a yellow oil which rapidly solidified. The *complex* crystallised from light petroleum in yellow prisms, m. p. 100—103° (decomp.), in 67% yield (Found: C, 32·35; H, 5·5; N, 3·25. $C_{12}H_{23}Cl_2NPt$ requires C, 32·2; H, 5·2; N, 3·15%).

Similarly prepared from Zeise's salt, $K[PtCl_3(C_2H_4)],H_2O$, were: *trans*-dichloro(ethylene)-(pyridine)platinum(II), *trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$, yellow needles (from ethanol), m. p. 110—114° (decomp.), 83% yield (Found: C, 22·9; H, 2·55; N, 3·9. Calc. for $C_7H_9Cl_2NPt$: C, 22·55; H, 2·45; N, 3·75%); and trans-*dichloro*(*ethylene*)(*γ-picoline*)*platinum*(II), *trans*-$[PtCl_2(C_2H_4)(4\text{-Me}\cdot C_5H_4N)]$, yellow needles from ethanol, m. p. 121—125° (decomp.), 87% yield (Found: C, 25·0; H, 2·95; N, 3·85. $C_8H_{11}Cl_2NPt$ requires C, 24·8; H, 2·85; N, 3·6%).

Determination of Dipole Moments.—These were determined as described previously.[24] The measurements and estimated values are recorded in Table 3. The margin of error is less than ±0·1 D for dipole moments >4 D, and less than ±0·2 D for dipole moments between 4 and 2·5 D. For dipole moments <2·5 D the margin of error will be greater than this, but is difficult to estimate. The errors in determining dipole moments of <2·5 D are largely due to the uncertainty in the magnitude of the atom polarisation which has been assumed to be 15% of the electron polarisation given in Table 3. ω = weight fraction of solute; $\Delta\varepsilon$ = difference between the dielectric constant of the solution and that of pure benzene; Δn = difference in refractive indices; Δv = difference in specific volumes; ${}_TP$ = total, ${}_EP$ = electron, and ${}_OP$ = orientation polarisations; μ = dipole moment.

TABLE 3. *Dipole moments of acetylene and olefin complexes of platinum*(II) *in benzene at 25°.*

No.	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^3\Delta n/\omega$	$-\Delta v/\omega$
1	*trans*-$[PtCl_2(Bu^tC{:}CBu^t)(C_5H_5N)]$			
	4·41	1·958	—	—
	4·882	1·963	—	—
	25·60	—	4·30	—
	35·44	—	4·19	—
	5·590	—	—	0·590
	6·980	—	—	0·573
2	[*trans*-$[PtCl_2(Bu^tC{:}CBu^t)(4\text{-Me}\cdot C_5H_4N)]$			
	6·397	2·588	—	—
	7·508	2·567	—	—
	22·73	—	3·33	—
	35·93	—	3·74	—
	2·891	—	—	0·588
	3·824	—	—	0·601
3	*trans*-$[PtCl_2(Bu^tC{:}CBu^t)(4\text{-Cl}\cdot C_5H_4N)]$			
	4·369	0·652	—	—
	5·430	0·695	—	—
	9·927	0·783	—	—
	25·70	—	3·96	—
	40·60	—	4·08	(0·58)
4	*trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$			
	4·603	4·438	—	—
	4·617	4·381	—	—
	36·29	—	7·80	—
	36·31	—	7·36	—
	5·915	—	—	0·626
5	*trans*-$[PtCl_2(C_2H_4)(4\text{-Me}\cdot C_5H_4N)]$			
	3·863	5·654	—	—
	4·060	5·669	—	—
	26·88	—	7·09	—
	31·80	—	6·86	—
	6·977	—	—	0·645
	7·223	—	—	0·568

No.	${}_TP$	${}_EP$	${}_OP$	μ (D)
1	260	91	155	2·75
2	323	90	220	3·3
3	157 *	97 *	45 *	1·5 *
4	368	73	284	3·75
5	475	76	388	4·35

* Calc. by using estimated values of densities and refractivities. Estimated values are given in parentheses. Those of $-\Delta v/\omega$ are needed only approximately and were estimated from experience of measurements on similar compounds.

Infrared Spectra.—The infrared spectra were measured with a Grubb–Parsons GS2A prism-grating spectrometer. For determination of $\nu_{C\equiv C}$ (stretching) the finely powdered solids were suspended in "Nujol," and for ν_{N-H} (stretching) a dilute solution of the complex in carbon tetrachloride was used.

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[*Received, August 25th,* 1960.]

[24] Chatt and Shaw, *J.*, 1959, 705.

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177. *Hydrous Tin*(II) *Oxide.*

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The preparation of pure hydrous tin(II) oxide [tin(II) hydroxide] has been investigated. The impossibility of preparing the compound free from both tin(IV) and anionic impurity by precipitation is demonstrated. Analysis indicates that the material cannot have any of the compositions previously suggested, and evidence given shows that the most probable composition is $5SnO,2H_2O$ [$Sn_5O_3(OH)_4$]. Hydrous tin(II) oxide is dehydrated in one stage at temperatures above 120° to give an orange amorphous material, not previously reported; this rapidly changes to blue-black tin(II) oxide on continued heating. The non-existence of the oxide Sn_3O_4 in the disproportionation product of tin(II) oxide is proved.

The precipitate [1,2] obtained by raising the pH of a solution of a stannous salt to about 10, by addition of any alkaline solution, is normally called tin(II) hydroxide. The chemical formula of the material is, however, not $Sn(OH)_2$ and throughout this work it is referred to more suitably as hydrous tin(II) oxide.

There are two conflicting reports of the chemical composition of the material, neither composition being founded on complete chemical analysis. Bury and Partington's [1] formula, $3SnO,2H_2O$, is based on analysis of total tin and water, and Weiser and Milligan's [2] formula, $2SnO,H_2O$, on the results of dehydration. Hydrous tin(II) oxide is dehydrated to blue-black tin(II) oxide when heated *in vacuo* or in a non-oxidising atmosphere, all the water being lost between 120° and 160°. At ~100° the material gradually becomes yellow and this colour darkens to orange; it is reported [2] that these colour changes are due only to changes in particle size. The disproportionation of the blue-black tin(II) oxide at higher temperatures has also been studied. Straumanis and Strenk [3] report that the disproportionation product is not a β-modification [2] of tin(II) oxide but a mixture of tin and tin(IV) oxide. Other authors [4,5] state that the products are tin and the oxide Sn_3O_4.

We have studied the composition of the hydrous tin(II) oxide precipitate, obtained the most likely formula for the material, and extended the data on its dehydration and on the disproportionation of tin(II) oxide.

Experimental

Preparation and Analysis.—Hydrous tin(II) oxide was prepared by addition of oxygen-free solutions of alkali or alkali carbonate to oxygen-free solutions of tin(II) sulphate,[6] under oxygen-free nitrogen, until the pH of the solution was between 10 and 12. The product was filtered off, washed either with deaerated distilled water or with alcohol followed by ether, and dried overnight *in vacuo* over various desiccants. Stannous and total tin were determined by Donaldson and Moser's method,[7] and water by heating the sample in a stream of oxygen and weighing the water in an anhydrone absorption tube. All water assays were checked by dehydration studies, under oxygen-free nitrogen, on a Stanton thermobalance.

Table 1 contains typical analyses of samples prepared with different precipitants. Average analytical data for 2 samples are reported in each case. Care must be taken when sodium hydroxide or sodium carbonate solutions are used as precipitants, because partial dehydration of the hydrous oxide to tin(II) oxide occurs if the pH rises above 12. Table 2 shows the effect of prolonged storage of hydrous tin(II) oxide *in vacuo* over various desiccants.

[1] (*a*) Bury and Partington, *J.*, 1922, **121**, 1998; (*b*) Proust, *J. Phys.*, 1800, **51**, 173; 1804, **61**, 338; Schaffner, *Annalen*, 1884, **51**, 168; Ditte, *Ann. Chim. Phys.*, 1882, **27**, 145; Britton, *J.*, 1925, **127**, 2120.
[2] Weiser and Milligan, *J. Phys. Chem.*, 1932, **36**, 3039.
[3] Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301.
[4] Spandau and Kohlmeyer, *Z. anorg. Chem.*, 1947, **254**, 65.
[5] Spandau and Ullrich, *Z. anorg. Chem.*, 1953, **274**, 271.
[6] Donaldson and Moser, *J.*, 1960, 4000.
[7] Donaldson and Moser, *Analyst*, 1959, **84**, 10.

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Samples prepared from solutions of tin(II) chloride dihydrate contained more tin(IV) as impurity than did those from tin(II) sulphate.

The change in composition of the precipitate—hydrous oxide or basic sulphate—with pH was studied by a series of preparations carried out under oxygen-free nitrogen in an air-tight compartment and with completely deaerated solutions. The preparations were as follows: N-Sodium hydroxide (varied amounts) was added to a solution of tin(II) sulphate [6] (5 g.) in 2N-sulphuric acid (20 ml.); the precipitate was washed with distilled water and dried overnight *in vacuo* over potassium hydroxide pellets. Tin and water were determined as above and sulphate by collecting any sulphur dioxide liberated in the water determination in a weighed soda–asbestos absorption tube. It is assumed that any sulphate present will decompose, giving tin(IV) oxide and sulphur dioxide by an internal oxidation–reduction, as does tin(II) sulphate.[6] Even if the reaction is not quantitative in the case of basic sulphates, it does give an indication of the amount of sulphate present in the precipitate and this is sufficient for the present work. Table 3 contains the analytical data for the precipitates obtained at different pH values.

TABLE 1. *Analytical data for hydrous tin*(II) *oxide.*

	Average results from analysis				Average results from analysis		
Precipitant	Stannous tin (%)	Total tin (%)	Water (%)	Precipitant	Stannous tin (%)	Total tin (%)	Water (%)
N-NaOH	79·5	81·0	4·63	Saturated aq. $NaHCO_3$	78·0	80·2	4·20
	78·4	81·4	4·42		78·3	80·4	4·23
Saturated aq. Na_2CO_3	79·1	81·0	4·20	2N-NH_3	79·3	82·1	4·41
	77·9	80·0	4·22		80·0	82·7	4·18

TABLE 2. *Effect of storage of hydrous tin*(II) *oxide* in vacuo *over various desiccants.*

	7 Days' storage		14 Days' storage	
Desiccant	Stannous tin (%)	Total tin (%)	Stannous tin (%)	Total tin (%)
P_2O_5.....	78·6	80·2	75·8	81·2
Conc. H_2SO_4	78·0	80·0	76·1	82·1
$Mg(ClO_4)_2$	78·2	80·1	77·8	81·4
KOH	78·1	80·2	76·1	82·2

TABLE 3. *Composition of the basic sulphate or hydrous tin*(II) *oxide with* pH.

pH of mother-liquor	Average results from analysis: Stannous tin (%)	Total tin (%)	Sulphate (%)	Water (%)	*X*-Ray diffraction powder pattern of ppt.
2·4	75·9	75·8	12·3	3·72	Basic sulphate
2·9	77·2	77·0	11·0	3·75	Basic sulphate
4·1	79·0	79·2	5·37	4·25	Some lines of basic sulphate and of hydrous oxide
4·2	80·9	80·9	3·99	4·63	Some lines of basic sulphate and of hydrous oxide
5·2	80·9	80·8	3·05	4·68	Some lines of basic sulphate and of hydrous oxide
6·3	80·1	82·5	1·77	4·83	Hydrous oxide
6·9	80·8	82·5	1·10	4·84	Hydrous oxide
9·6	80·0	82·1	0·63	4·94	Hydrous oxide
10·1	80·1	82·2	0·63	4·92	Hydrous oxide
10·6	80·8	82·6	0·61	4·98	Hydrous oxide
11·7	79·5	82·2	traces	4·97	Hydrous oxide

Hydrous tin(II) oxide can be prepared in a crystalline form by the hydrolysis of some basic tin(II) salts. When basic tin(II) nitrate [8] is stored for a few days under deaerated distilled water, yellow nuggets of hydrous tin(II) oxide are deposited. These nuggets contain some tin(IV) and nitrate as impurity and although they are suitable for study by *X*-ray diffraction [9] they are less pure than samples prepared by precipitation.

Thermal Dehydration of Hydrous Tin(II) *Oxide.*—The dehydration was followed on a Stanton thermobalance in an atmosphere of oxygen-free nitrogen. The water is lost in one stage at

[8] Donaldson and Moser, in the press.
[9] Donaldson, *Acta Cryst.*, in the press; Donaldson, Moser, and Simpson, following paper.

temperatures above 120°, but the initial dehydration product is an orange material and not blue-black tin(II) oxide as previously reported.[2] We thus show that Weiser and Milligan wrongly reported that the yellow and the orange colour were connected with the particle size of the hydrous oxide. The material contains no more tin(IV) than was present in the hydrous oxide from which is was prepared and contains no water. The composition of the material is, therefore, SnO. Its *X*-ray diffraction powder pattern which consists of a single diffuse band (at 2·97 Å) shows that the material is amorphous. The orange material, unlike the blue-black and the red [10] modifications of the monoxide, is converted into tin(IV) oxide by a few days' contact with air, in agreement with the small particle size of an amorphous solid.

The disproportionation of tin(II) oxide was studied by *X*-ray-diffraction techniques at the decomposition temperature (385°). The powder pattern above this temperature contains only lines due to tin(IV) oxide; there is no evidence for the presence of a new phase Sn_3O_4. When the sample is cooled below 230° additional lines appear in the pattern but these are all assignable to the tin phase which solidifies at this temperature.

TABLE 4. *X-Ray diffraction powder data for hydrous tin(II) oxide.*

d (Å)	Rel. intensity	*d* (Å)	Rel. intensity	*d* (Å)	Rel. intensity	*d* (Å)	Rel. intensity
6·02	vw	2·42	mw	1·67	m	1·304	vw
5·68	vw	2·29	w	1·63	m	1·282	vvw
5·01	vvw	2·00	vvw	1·568	m	1·244	w
4·60	vvw	1·94	m	1·539	m	1·207	vvw
3·55	s	1·92	m	1·503	vw	1·200	vvw
3·31	m	1·83	w	1·476	m	1·188	s
3·00	s	1·78	s	1·427	vvw	1·162	vvw
2·82	vs	1·77	w	1·398	mw	1·149	vvw
2·52	mw	1·74	w	1·341	vw	1·123	m

Table 4 contains the *X*-ray diffraction powder pattern of hydrous tin(II) oxide obtained by using 11·64 cm. cameras and a Philips *X*-ray diffractometer with filtered Cu-K_α radiation. The data improve upon those in the A.S.T.M. index (No. 7-194) in content and accuracy. The powder pattern of a freshly prepared paste of hydrous tin(II) oxide is identical with that of the dried material, showing that drying does not lead to appreciable quantities of a new phase.

DISCUSSION

In the analysis of hydrous tin(II) oxide all previous workers have relied on determination of total tin and neglected the possible presence of tin(IV). However, the analytical data above show that even samples prepared in the complete absence of elemental oxygen contain about 2% of tin(IV). The buff colour of the dried material is presumably due to the presence of this impurity. The results (Table 2) strongly suggest that it is impossible to prepare, by precipitation, a sample of hydrous tin(II) oxide which is free from both tin(IV) and sulphate. Sulphate contamination of over 1% occurs up to a pH of about 7, and appreciable oxidation of tin in the sample occurs from pH 6·3. The only explanation of the formation of tin(IV) in experiments under nitrogen and in vacuum-desiccators (Table 3) seems to be reduction of water (hydroxyl) by the bivalent tin. Measurement of the potential of a platinum electrode in a solution of pure tin(II) sulphate in water with increasing pH shows a sharp change of about 0·1 v between pH 6·0 and 6·2. This is due to the initial rise in tin(IV) concentration from traces to about 2%, a result in agreement with those in Table 3.

Derivation of a formula for the material is difficult for three reasons: (1) It is not certain whether the impurities form a separate phase or whether they are in some way distributed homogeneously throughout the hydrous oxide phase. For the stannic tin impurity, homogeneous distribution seems more likely because of the darkening of colour with increase in tin(IV) content. All precipitates of hydrous tin(II) oxide are white when freshly prepared and become buff only on drying. This suggests that the stannic tin occupies sites in the hydrous oxide lattice and may in part arise from the internal reaction,

[10] Partington and Moser, *Nature*, 1944, **154**, 643.

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$2Sn^{2+} + 2OH^- \longrightarrow Sn^{4+} + 2O^{2-} + H_2$. (2) It is not certain how much of the water is associated with impurity phases but the one-stage dehydration suggests that all of the water is associated with one phase and this must be the hydrous oxide phase. (3) It is not certain how much of the tin is associated with the traces of sulphate impurity.

It is obvious, however, from the fact that the amount of water in the sample never exceeds 5%, that the formulæ $3SnO,2H_2O$ (requiring 8·18% of water) [1a] and $2SnO,H_2O$ (requiring 6·26% of water) [2] are inadmissible. A formula containing less water is more likely. If we make the assumptions (*a*) that the tin(IV) present occupies sites in the hydrous oxide lattice and (*b*) that the traces of sulphate are essentially sorbed impurities, the tin and water percentages for the last four samples in Table 3 become: 83·7, 5·00; 83·5, 5·00; 83·4, 5·03; 83·4, 5·04. From these figures it seems that the most probable composition of hydrous tin(II) oxide is $5SnO,2H_2O$ (requiring 83·7% of tin, 5·07% of water). Further support for the suggested formula comes from unit-cell and density data; [9] the probable contents of the large triclinic cell are more nearly a multiple of $5SnO,2H_2O$ than of any other simple formula. Finally, in view of the similarity between the compounds of tin and lead, the fact that the composition of hydrous lead(II) oxide is reported [11] as $5PbO,2H_2O$ may be taken as evidence for the suggested formula.

The gradual yellowing and darkening of hydrous tin(II) oxide heated in the absence of oxygen, as reported by Weiser and Milligan,[2] was observed and may indicate the onset of dehydration. Hydrous tin(II) oxide is dehydrated completely, to give an orange amorphous material which, from its colour, is presumably related to the red modification of tin(II) oxide but is converted, if further heated, into the more stable blue-black tin(II) oxide before sizeable crystals of the red form can develop. The disproportionation products of tin(II) oxide are confirmed as tin and tin(IV) oxide, as reported by Straumanis and Strenk.[3] This disproportionation is an example of the internal oxidation–reduction common in oxygen-containing tin(II) compounds. In the case of tin(II) oxide the material is simultaneously oxidised to the very stable tin(IV) oxide and reduced to tin metal. Spandau and Kohlmeyer [4] postulated the existence of the oxide Sn_3O_4 to avoid an apparent phase-rule difficulty. The difficulty, however, only arises because of the analytical method which they used. Their method depended on the mechanical separation of tin by sieving, but failure to remove all of the tin results in its inclusion in the analytical report as SnO. Moreover, in some cases they found it impossible to remove the metallic tin, and analyses were obtained by weighing the residue, which would not dissolve in concentrated hydrochloric acid, and assuming it to be the total original tin(IV) oxide. The tin and tin(II) oxide percentages were then obtained by difference, with allowance for the oxygen originally present in the SnO sample. This procedure is meaningless, because any original tin(IV) oxide small enough to be dissolved or reactive enough to be reduced (by dissolution of metal) during the hydrochloric acid extraction necessarily appears as tin(II) oxide. The fact that *X*-ray-diffraction studies indicate the absence of lines due to tin(II) oxide or to a possible new phase, Sn_3O_4, proves that this oxide does not exist in the decomposition products of tin(II) oxide, either as a mixed oxide or as a separate phase.

One of us (J. D. D.) is grateful to D.S.I.R. for a Research Grant.

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[11] Clark and Tyler, *J. Amer. Chem. Soc.*, 1939, **61**, 58.

178. *Red Tin(II) Oxide.*

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The preparation of a red modification of tin(II) oxide is described and the exact conditions under which it can be obtained are reported. The stability of the material is discussed, and the *X*-ray diffraction powder and unit-cell data are given.

A metastable red modification of tin(II) oxide has been reported [1-3] by some workers; others [4,5] state that they were unable to repeat the preparations. The purpose of this work is to set down the exact conditions under which the red form of tin(II) oxide can be prepared by dehydration of a hydrous tin(II) oxide [6] or basic salt suspension. The *X*-ray diffraction powder and unit-cell data of the material are also listed.

Experimental

Preparation.—Two methods, based on the work of Roth [1] and of Fremy,[2] have been used for the preparation of red tin(II) oxide. The optimum conditions are here given along with the limits of concentration of the variable components.

Preparation based on Roth's method. Tin(II) chloride dihydrate (25 g.) of analytical reagent grade is dissolved in concentrated hydrochloric acid (20 ml.) and water (10 ml.), and the solution cleared by warming over tin metal. Hydrous tin(II) oxide is precipitated by addition of a saturated solution of sodium hydrogen carbonate until evolution of carbon dioxide ceases. A solution of sodium phosphite (0·3 g.) in N-acetic acid (125 ml.) is then added, and the pH adjusted to 5—6 by addition of a saturated solution of sodium hydrogen carbonate or of 0·1N-hydrochloric acid as necessary. The suspension is heated, with rapid stirring, under an atmosphere of oxygen-free nitrogen, on a bath at 102° (boiling $CaCl_2$ solution) until most of the precipitate has been converted into red oxide. The oxide is separated from the less dense hydrous oxide or basic chloride, firstly by decantation, and finally by passing the mixture through a cascade filter in a continuous flow of water. The cascade filter consists of 5 cloth filters of mesh size from 0·38 to 0·013 mm. The basic salt or hydrous oxide is peptised and washed away, leaving pure red tin(II) oxide on the filter. The product is dried *in vacuo* over potassium hydroxide pellets.

The effects of varying phosphite concentration, pH, and volume of acetic acid in the preparative mixture are as follows:

Red tin(II) oxide is obtained if the phosphite concentration is between 0·17 and 1·1 g. in 125 ml. of N-acetic acid. Above the upper limit no oxide formation occurs, and below the lower limit blue-black tin(II) oxide is formed. The colour of the sample ranges from purple to very red as the phosphite concentration increases, but the time for initial red oxide formation also increases from 45 min. at 0·17 g. to 4¾ hr. at 1·1 g. of phosphite. The production of a purple material indicates the presence of some blue-black oxide; this was confirmed by the presence of the strongest reflection of this oxide (2·97 Å) in the powder pattern of the purple material.

Partington and Moser [3] prepared red tin(II) oxide by a similar method but used sodium hypophosphite instead of sodium phosphite. It has been found, however, that only old samples of hypophosphite, containing phosphite impurity, give rise to red oxide in the preparation. In fact, sufficient hypophosphite must be used so that the phosphite content falls within the range 0·17—1·1 g. in the preparative mixture.

The pH of the suspension was varied by addition of varying amounts of solid sodium hydrogen carbonate, and it was found that red tin(II) oxide could only be obtained between

[1] Roth, *Jahrb. prakt. Pharm.*, 1845, **10**, 381.
[2] Fremy, *Compt. rend.*, 1842, **15**, 1108; *Ann. Chim. Phys.*, 1844, **12**, 460.
[3] Partington and Moser, *Nature*, 1944, **154**, 643.
[4] Bury and Partington, *J.*, 1922, **121**, 1998.
[5] Weiser and Milligan, *J. Phys. Chem.*, 1932, **36**, 3039.
[6] Donaldson and Moser, preceding paper.

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the pH limits 4·9—6·2. In a suspension of pH <4·9 no oxide formation occurs, and only blue-black oxide is obtained from a suspension with pH >6·2.

Variation of acetic acid concentration has little effect, since red tin(II) oxide can be obtained from suspensions containing from 0 to 300 ml. of N-acetic acid. The yield of red oxide, however, decreases if the acetic acid concentration is less than 80 ml. or greater than 200 ml. in the preparative mixture. The main function of the acetic acid is apparently to produce a suitable buffer solution.

Preparation based on Fremy's method. A solution of tin(II) chloride dihydrate is prepared and cleared as in Roth's method, and hydrous tin(II) oxide is precipitated by addition of an aqueous solution of ammonia (*d* 0·880; 1 : 1) until the pH is about 10. The precipitate is allowed to settle, the excess of liquid decanted off, and the suspension transferred to a 4″ evaporating dish which is heated on a boiling-water bath without stirring until red oxide begins to be formed near the sides of the dish. A little of the suspension from the centre of the evaporating dish is transferred to a larger preheated dish, and this is rotated slowly at a slight angle until a uniform film is obtained. The dish is replaced on the water-bath and heated until the film becomes red. The product, a fine powder, is removed by a jet of water, washed by decantation, and dried as before.

This preparation does not depend on the concentration of any of the components in the mixture, but is sensitive to experimental conditions. Care must be taken in transferring the suspension from one evaporating dish to another since any oxide crystals transferred will act

X-Ray powder data for red tin(II) *oxide.*

d (Å)	R.I.*	Index of refl.	$d_{calc.}$	*d* (Å)	R.I.*	Index of refl.	$d_{calc.}$	*d* (Å)	R.I.*	Index of refl.	$d_{calc.}$
5·56	vvw	002	5·56	1·888	vw	220	1·883	1·342	vvw	043	1·339
3·71	vvw	102	3·72	1·857	s	204	1·855	1·251	vw	400	1·250
3·58	w	111	3·57	1·773	mw	130	1·781	1·239	vw		
3·12	vvs	112	3·12	1·681	w	223	1·681	1·213	vw		
2·86	vw	020	2·86	1·662	vw	116	1·663	1·183	vw		
2·78	mw	004	2·78	1·610	vw	133	1·608	1·141	vw		
2·50	w	200	2·50	1·540	w	312	1·539	1·095	w		
2·25	vw	023	2·26	1·429	mw	040	1·430	1·028	vvw		
1·994	vvw	024	1·994	1·393	vw	{ 008 { 042	1·390 1·385 }				

* R.I. = relative intensity.

as nuclei for the formation of blue-black oxide. This stable oxide is also obtained if the film in the second evaporating dish is not uniform or too thick, because continued moistening and heating of freshly prepared red oxide converts it into the blue-black form.

Purity and Stability of Red Tin(II) *Oxide.*—Analysis for stannous tin and total tin by Donaldson and Moser's method [7] for three samples of red oxide prepared by Roth's method gave 87·5, 88·0; 87·6, 88·1; 87·4, 88·0%; and for three samples from Fremy's method gave, 86·1, 86·6; 86·0, 86·9; 86·1, 86·7%. [Calc. for SnO: Sn(II), 88·1%]. Products produced by Fremy's method are obviously contaminated by basic salts. No band attributable to either water or hydroxyl appears in the infrared spectrum of red tin(II) oxide.

Red tin(II) oxide is stable in air up to about 270°, possibly owing to the presence of a thin protective coating of tin(IV) oxide. The change from the red modification of tin(II) oxide to the blue-black form has been studied in a non-oxidising atmosphere by using high-temperature *X*-ray diffraction techniques; it was found that the change occurred at temperatures varying with the age of the sample.

Red tin(II) oxide can also be converted into the blue-black modification by mechanical pressure at room temperature, by treatment with strong alkali, or by contact with the stable modification, and must thus be considered metastable.

Crystallography.—Careful control of Roth's preparation by allowing a little red oxide to be formed as usual, decanting from this, and stirring the decanted suspension slowly for 2 hr. at 60° yields crystals suitable for study by *X*-ray diffraction.

Crystal data: red SnO, $M = 134·7$, orthorhombic, $a = 5·00 \pm 0·01$, $b = 5·72 \pm 0·01$,

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$c = 11{\cdot}12 \pm 0{\cdot}02$ Å, $U = 318{\cdot}0$ Å^3, $D_m = 5{\cdot}56$ g./c.c. (by displacement of water), $Z = 8$, $D_c = 5{\cdot}63$ g./c.c., space-group $Pbcn$ D_{2h}^{14} (No. 60), filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about a and b.

The Table contains the *X*-ray diffraction powder data for red tin(II) oxide obtained by using 11·64 cm. cameras and a Philips *X*-ray diffractometer with filtered Cu-K_α radiation. The spacings longer than 1·25 Å have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions.

Discussion

It is apparent from the preparation by Fremy's method that the material which is dehydrated to red tin(II) oxide is either hydrous tin(II) oxide or a basic tin(II) chloride. Any ammonia present is driven off during the preparation, thus lowering the pH of the suspension. It was found that the pH of the suspension from which red oxide could be obtained was between 5·5 and 6.

Presumably, the same material is responsible for the production of red oxide in Roth's preparation. In this case the pH is kept at about 6 by a sodium acetate–acetic acid buffer. The effect of phosphite on Roth's method indicates that both dehydration and oxide transformation can be retarded by a negative catalyst. Work is in progress to determine the exact composition of the precursor of the red oxide and to study the effect of the phosphite in the dehydration. All attempts to prepare red tin(II) oxide from pure tin(II) sulphate [8] or from hydrous oxide precipitated from a nitrate solution have failed, and although small quantities of red tin(II) oxide can be obtained from tin(II) bromide, it seems that the presence of chloride ion is essential for the production of good yields of red tin(II) oxide.

The red modification of tin(II) oxide is certainly metastable at ordinary temperatures and it is possible that the true stability range of the material lies above the disproportionation [6,9] temperature of tin(II) oxide, *viz.*, 385°.

Comparison of the *X*-ray and unit-cell data of red tin(II) oxide with those reported for yellow lead(II) oxide [10] indicates that the two materials cannot have the same structure. Work is in progress to determine the structure of red tin(II) oxide.

We thank Professor J. R. Partington and Dr. H. F. W. Taylor for their help in the initial stage of this work. One of us (W. B. S.) is grateful to the International Tin Research Council for a maintenance grant.

Chemistry Dept., The University, Old Aberdeen. [*Received, October 7th*, 1960.]

[7] Donaldson and Moser, *Analyst*, 1959, **84**, 10.
[8] Donaldson and Moser, *J.*, 1960, 4000.
[9] Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301.
[10] Byström, *Arkiv Kemi, Min., Geol.*, 1943, **17**, *B*1; *Chem. Zentr.*, 1944, I, 343.

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179. *Sorption of Mixtures, and Selectivity in Alkylammonium Montmorillonites. Part I. Monomethylammonium Bentonite.*

By R. M. Barrer and G. S. Perry.

A study has been made of the sorption of single and of binary mixtures of hydrocarbons by methylammonium montmorillonite. This has been combined with *X*-ray measurements of the *c*-spacing in presence of various amounts of sorbed hydrocarbons, which have demonstrated interlamellar sorption for benzene and n-heptane, but its absence for cyclohexane or iso-octane (2,2,4-trimethylpentane). Three kinds of mixture were then examined: one having both components intercalated; three having one component intercalated; and one having neither component intercalated. The middle group shows true molecular-sieve behaviour, modified by some competitive adsorption on external crystallite surfaces.

Interlamellar sorption of benzene by the clay derivative occurs only above a threshold pressure, and some phenomena akin to nucleation of a new phase can be observed. Such behaviour was not found for n-alkanes. Monomethylammonium montmorillonite sorbs cyclohexene irreversibly and appears to catalyse its polymerisation.

It has been shown, by using a bentonite * having a B.E.T. area to nitrogen of about 21·7 m.²/g., that a very great increase in the effective area of the sorbent may be achieved simply by replacing the inorganic ions by $Me{\cdot}NH_3^+$, $Me_2NH_2^+$, Me_3NH^+, Me_4N^+, and Et_4N^+. As a result the outgassed clay copiously sorbed atmospheric gases, and also many hydrocarbons which were not sorbed to any extent before ion-exchange.[1,2,3] The clays have developed a permanent interlamellar porosity which is responsible for these effects. They may be very effective in resolving molecular mixtures,[4] the components of which penetrate with different selectivities into the interlamellar spaces. In the present paper an account is given of these selectivities through the study of equilibria between binary mixtures of vapours in the vapour phase in and on porous-clay crystals having methylammonium as the interlamellar ion. In this way quantitative understanding of molecular-sieve behaviour may be obtained, and thus means for predicting the selectivity towards other mixtures. This information can be correlated with similar information reported in the following paper for a tetramethylammonium bentonite, which has different porosity characteristics; and with the behaviour of dimethyl dioctadecylammonium bentonite (Bentone-34), useful in gas chromatography [5,6] and possessing some interesting properties as a sorbent.[7]

Adsorption isotherms of mixtures cannot in general be predicted from those of the individual pure components.[8,9] Accordingly selectivity and its causes can be adequately established only by studying sorption equilibria of mixtures. Compared with the information available on the uptake of single species, mixture sorption is a rather neglected field, of which understanding has so far been limited. Accordingly, there is need for various studies of the kind now reported.

* The term " bentonite " can be used to describe montmorillonite clays that may not be completely pure.

[1] Barrer and MacLeod, *Trans. Faraday Soc.*, 1955, **51**, 1290.
[2] Barrer and Reay, Proc. 2nd Internat. Congress of Surface Activity, 1957, Butterworths, London, p. 79.
[3] Barrer and Reay, *Trans. Faraday Soc.*, 1957, **53**, 1253.
[4] Barrer and Hampton, *Trans. Faraday Soc.*, 1957, **53**, 1462.
[5] White, *Nature*, 1957, **179**, 1075.
[6] White and Cowan, *Trans. Faraday Soc.*, 1958, **54**, 557.
[7] Barrer and Kelsey, unpublished work.
[8] Lewis, Gilliland, *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 1153, 1157, 1160.
[9] Benedek and Szepesy, *Acta Chim. Acad. Sci. Hung.*, 1958, **14**, 31.

Experimental

The apparatus for measuring the sorption and intercalation of vapour mixtures has been described elsewhere.[4] It was, however, modified by connecting the freezing-out bulb F_2 [4] to the doser volume through a mercury cut-off. This allowed isolation of the added hydrocarbon, required to restore the original composition of the vapour mixture. When a further dose of the mixture is added the possibility of diluting the source mixture is thereby avoided.

The sorbates studied in this and in the following paper, their quality, and some physical characteristics of importance for this work, are recorded in Table 1.[10] The methylammonium bentonite was that used earlier.[4] In general, analysis of binary mixtures was readily effected by refractometry. For n-hexane–iso-octane * mixtures, however, gas–liquid partition chromatography was employed, the areas under the curves for the separated components being determined as suggested by Keulemans,[11] and the instrument calibrated by means of the pure n-hexane and iso-octane.

c-Spacings of the crystals of sorbent were measured from powder photographs obtained at 24° with a Hilger and Watts HRX *X*-ray unit and filtered Cu-K_α radiation. A flat plate camera was employed, and the specimen-to-film distance was 10 or 11 cm. Measurements were made on samples contained in Pyrex capillaries.[3] Before introduction of sorbate, the clay was outgassed at 100° for 8—10 hr. under a high vacuum, a condition known to remove virtually all sorbed water.[1] After equilibration with the required pressure of sorbate vapour the capillaries were sealed and were ready for *X*-ray-diffraction studies.

Table 1. *Characteristics of the sorbates.*

Compound	Origin and quality	B. p.	n_D	Latent heat of vaporisation (kcal./mole)	Saturation v. p. at 80° (cm.)
Benzene	" AnalaR "	80·1°	1·5011	7·36 (80°)	75·5
Cyclohexane	For spectroscopy (B.D.H.)	80·8	1·4263	7·89 (25°)	74·3
Cyclohexene	Reagent (B.D.H.)	82·9	1·4467	—	68
n-Heptane	Engine standard	98·4	1·3876	7·71 (90°)	42·7
n-Hexane	N.C.L., Teddington	68·7	1·3751	6·92 (60°)	106·2
Iso-octane	Engine standard	99·2	1·3916	8·39 (25°)	50·5
n-Perfluoroheptane	Some impurities (Minnesota Mining and Mfg. Co.)	82·5	—	—	—

Table 2. B.E.T. *monolayer values*, v_m.

Sorbate	Mol. area (Å²) of sorbate	v_m value (cm.³ at s.t.p./g.*) This work	Ref. 13
Benzene	25	23·3	27·3
n-Heptane	51	7·6	10·9
n-Hexane	44	8·7	—
Cyclohexane	46	3·5	5·0
Iso-octane	52	1·9	2·1

* All sorptions refer to 1 g. of outgassed sorbent.

X-Ray Measurements.—The *c*-spacing of outgassed monomethylammonium bentonite was 11·6 ± 0·1 Å, and was confirmed on samples derived both from Na- and Ca-rich parent clays. In air the *c*-spacing rose to 12·2 Å, and at saturation with water vapour the value was 12·8 Å. The last value agrees with those reported elsewhere [12,13] and it seems probable that the value of 12·0 Å found by Barrer and Reay [2,3] refers to a sample containing some sorbed water. The figure of 11·6 Å gives a free distance of 2·2 ± 0·1 Å between surfaces of adjacent aluminosilicate lamellæ.

* The material described, for brevity, by its commercial name " iso-octane " is 2,2,4-trimethylpentane.

[10] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.
[11] Keulemans, " Gas Chromatography," Reinhold Publ. Corp., New York, 1957.
[12] Bradley, *J. Amer. Chem. Soc.*, 1945, **67**, 975.
[13] Greene-Kelly, *Trans. Faraday Soc.*, 1956, **52**, 1281.

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Interesting variations in the *c*-spacings of the lattice in presence of several sorbates are shown as a function of relative pressure in Fig. 1*a* and of amount sorbed in Fig. 1*b*. The amount sorbed was interpolated from previous data [3] by assuming that it was a function only of relative pressure, p/p_0, the temperature coefficients of sorption in terms of p/p_0 being small. The figures show a progressive increase in *c*-spacing in presence both of benzene and of n-heptane, demonstrating clearly the interlamellar uptake. On the other hand, there is a little swelling only at high relative pressure (in the region of capillary condensation) for cyclohexane, and none at all for iso-octane. Since the dimensions of each molecule are such that intercalation would cause substantial lattice expansion, for neither sorbate when alone is the interlamellar porosity appreciably accessible. Although a molecular-sieve effect is thus demonstrated quite conclusively for the pure sorbates, it is possible that when lattice expansion has occurred in presence of benzene or heptane, cyclohexane or iso-octane might now have some access to the interlamellar pores. This can be considered only by study of actual mixtures.

Sorption of Mixtures.—Isotherms of the following mixtures, over a range of compositions,

FIG. 1.

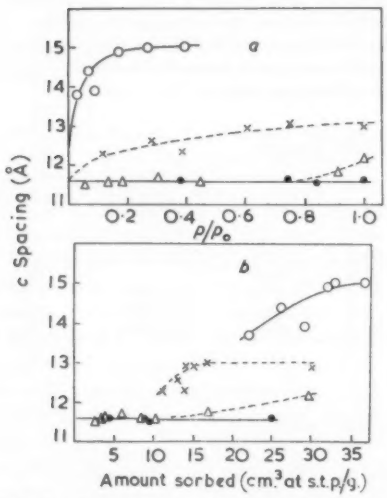

FIG. 2.

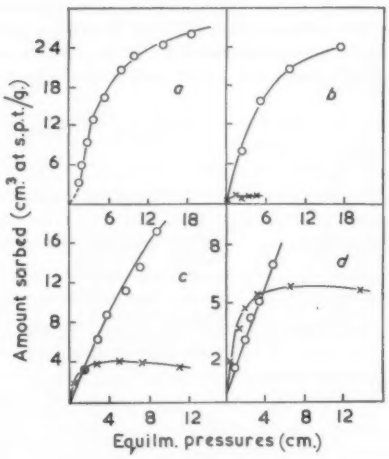

FIG. 1. (*a*) *c-Spacings at room temperature as a function of relative pressures of sorbates with which the complexes are in equilibrium.*

(*b*) *c-Spacings at room temperature as functions of amounts sorbed.*

○, *Benzene*; ×, *n-heptane*; △, *cyclohexane*; ●, *iso-octane.*

FIG. 2. (*a*) *The benzene isotherm showing evidence of a threshold pressure for small amounts sorbed.*

(*b*), (*c*), (*d*) *Isotherms for benzene* (○) *and n-heptane* (×) *from mixtures of initial compositions* (*b*) 0·89, (*c*) 0·67, *and* (*d*) 0·50 *mol. fraction of benzene.*

have been measured at 80°, the figures quoted giving the compositions of the mixtures in terms of the mole fractions of the first-named component: Benzene–n-heptane 0·89, 0·67, 0·50, 0·30, 0·16. Benzene–cyclohexane 0·80, 0·50, 0·20. n-Heptane–cyclohexane 0·64, 0·50, 0·21. Cyclohexane–iso-octane 0·69, 0·25. n-Hexane–iso-octane 0·71, 0·53, 0·36.

The sorption isotherms of each pure component were measured in addition, and equivalent B.E.T. monolayer values, v_m, recorded in Table 2, are, in view of uncertainties in the method, and differences in the samples of sorbent used, in reasonable agreement with values obtained by Reay.[14] The low v_m values for cyclohexane and iso-octane support the *X*-ray evidence that these sorbates are not appreciably intercalated. Benzene gives, as observed previously, much the largest v_m value, compatible with its vertical orientation between lamellæ.[2,3]

[14] Reay, Ph.D. Thesis, London, 1956.

Figs. 2*b*—5*c* show the isotherms at equilibrium of each component for some of the mixtures listed above. The mixtures chosen are of three kinds: (i) those in which both pure components undergo interlamellar sorption (benzene–n-heptane); (ii) those in which only one pure component undergoes interlamellar sorption (benzene–cyclohexane; n-heptane–cyclohexane; n-hexane–iso-octane); (iii) those in which neither pure component undergoes inter-lamellar sorption (cyclohexane–iso-octane). The characteristics of the isotherms, and the selectivities, can be discussed with this behaviour in mind.

Discussion of Isotherms.

(a) *Benzene–n-Heptane.*—Unusual features are shown by the benzene–heptane mixtures sorbed by the methyl ammonium clay. The change-over in order of selectivity observed by

Fig. 3.

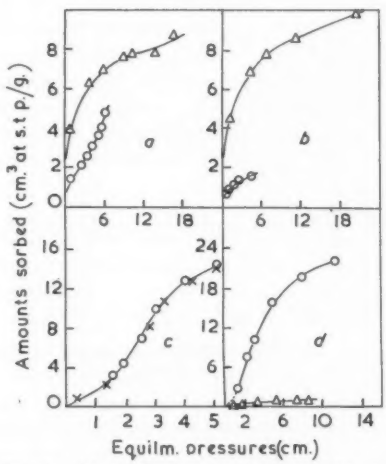

Fig. 4.

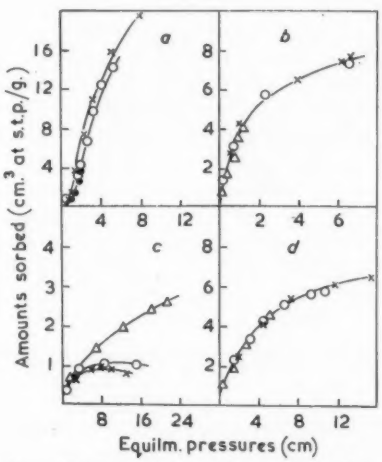

Fig. 3. (*a*), (*b*) *Isotherms for benzene* (○) *and n-heptane* (△) *from mixtures poor in benzene* [*mol. fraction* (*a*) 0·30, (*b*) 0·16].

(*c*) *Reproducibility of isotherm for benzene in a benzene–cyclohexane mixture* (*benzene mol. fraction* 0·5), *showing tendency to a threshold pressure for benzene.* ○ *1st,* × *2nd run.*

(*d*) *Isotherms for benzene and cyclohexane, showing selectivity to benzene* (*benzene mol. fraction* 0·80). ○ *Benzene*; △ *cyclohexane.*

Fig. 4. (*a*) *The isotherms for benzene from mixtures with cyclohexane, showing that the benzene sorption is little affected by presence of cyclohexane. Benzene mol. fraction*: × 0·80; ○ 0·50, ● 0·20.

(*b*) *and* (*d*) *Behaviour similar to that shown in Fig.* 4 (*a*), *for* (*b*) *n-heptane in mixtures with cyclohexane, and* (*d*) *for n-hexane in mixtures with iso-octane.* (*b*) *n-Heptane mol. fraction*: × 0·64, △ 0·54, △ 0·2. (*d*) *n-Hexane mol. fraction*: × 0·71, ○ 0·53, △ 0·36.

(*c*) *The isotherms of cyclohexane in mixtures with n-heptane, strongly modified by the latter. Cyclohexane mol. fraction*: △ 0·77, ○ 0·50, × 0·36.

Barrer and Hampton [4] is confirmed (Figs. 2*c* and *d*), as is the curious, nearly linear form of the benzene isotherms when the feed mixtures contained 0·33 and 0·50 mol. of n-heptane. The isotherm of pure benzene (Fig. 2*a*) approaches type V in Brunauer's classification,[15] a shape also given by ammonia in natural clay.[1,16]. In the latter case it was suggested that the first additions of sorbate are restricted to external surfaces of the crystals, and that only after a threshold pressure of sorbate vapour has been reached is there penetration between the lamellæ.[1] This explanation can now be applied to the uptake of benzene by the

[15] Brunauer, "The Adsorption of Gases and Vapours," Oxford Univ. Press, 1945, p. 150.
[16] Barrer and MacLeod, *Trans. Faraday Soc.*, 1954, **50**, 980.

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methylammonium clay. On the other hand, isotherms of n-heptane do not show a threshold pressure, and n-heptane must be presumed to penetrate between lamellæ from the lowest pressures. When it is intercalated, benzene expands the lattice considerably more than n-heptane (Figs. 1*a* and *b*) (the energy requirement for which may account for its initial exclusion), and its intercalation then takes place copiously and the order of selectivity between benzene and n-heptane is reversed. Benzene uptake thus involves phenomena akin to the nucleation of a new phase in a matrix of the old.

At points where the isotherms cross (Figs. 2*c* and *d*), neither component is selectively sorbed, and this composition has been called the " adsorption azeotrope " (Reeds and Kammermeyer [17]). The adsorption azeotropic compositions occur at different pressures

FIG. 5.

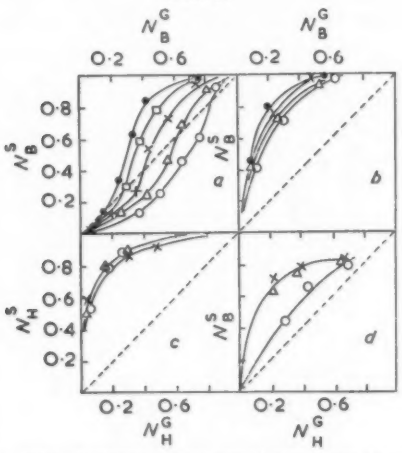

FIG. 6.

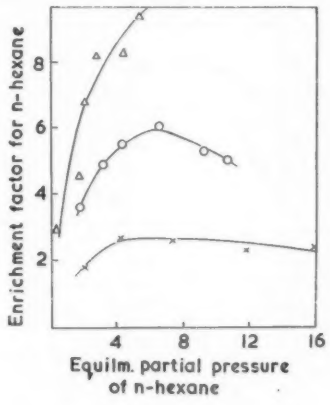

FIG. 5. *Mol. fractions of first-named constituent in sorbed phases as a function of mol. fraction in the gas phases, at equilibrium.*

(a) Benzene–n-heptane. (b) Benzene–cyclohexane. (c) n-Heptane–cyclohexane. (d) n-Hexane–iso-octane.

Individual curves refer to total equilibrium pressures as follows: ○ 2·5, △ 5·0, × 10, □ 15, ● 20 cm. *For individual points on the curves, mol. fractions of the first-mentioned constituent in the initial mixtures were, reading upwards*: (*a*) 0·16, 0·30, 0·50, 0·67, 0·89; (*b*) 0·21, 0·50, 0·64, 0·80; (*c*) 0·20, 0·50, 0·80; (*d*) 0·31, 0·53, 0·71.

FIG. 6. *Enrichment factors at 80° as functions of partial pressure of n-hexane in mixtures with iso-octane. Mol. fractions of n-hexane in the original mixtures*: × 0·71, ○ 0·53, △ 0·36.

of benzene and n-heptane for different initial compositions. For mixtures both richer and poorer in benzene (Fig. 2*b*; and Figs. 3*a* and 3*b* respectively) adsorption azeotropic compositions cannot readily be located if they occur at all.

(b) *Benzene–Cyclohexane.*—In this mixture, only benzene is intercalated in the pure state (see above). The important question arises whether, when the lattice has once been expanded by the benzene, the cyclohexane will also be able to penetrate between lamellæ. A rather good adsorption-chromatographic separation of this pair by the methylammonium clay was reported;[4] some mixture isotherms are shown in Fig. 3*c* and *d* and Fig. 4*a*. The very great selectivity towards benzene is apparent from Fig. 3*d*, and the type V character of the isotherms of benzene in the mixtures is seen clearly in Fig. 3*c*.

When the isotherms for benzene in three different mixtures with cyclohexane are plotted on the same diagram (Fig. 4*a*), all three are seen to be nearly superposable. Cyclohexane, whether at mol. fraction 0·80, 0·50, or 0·20, offers little competition for sorption sites.

[17] Reeds and Kammermeyer, *Ind. Eng. Chem.*, 1959, **51**, 707.

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It thus appears that even when benzene has entered and expanded the lattice of the clay crystals there is little or no tendency for cyclohexane also to enter.

(c) *n-Heptane–Cyclohexane; n-Hexane–Iso-octane.*—In both these mixtures it is only the n-alkane which, in the pure state, undergoes interlamellar sorption (see above). For the first mixture the isotherms of n-heptane are seen to be almost superposable in three mixtures for which the mol. fractions of cyclohexane are 0·36, 0·50, and 0·79 respectively (Fig. 4*b*). Thus, cyclohexane does not effectively compete with n-heptane for sorption sites between the lamellæ. On the other hand, as the n-heptane content increases the already small sorption of cyclohexane is progressively decreased (Fig. 4*c*). It can be seen that both molecular species are in competition for the small external surface of the clay crystals, and that only n-heptane has access to the much more numerous interlamellar sorption sites. A similar situation is found for hexane–iso-octane mixtures, the hexane isotherms being independent of varying mol. fractions of iso-octane (Fig. 4*d*).

(d) *Cyclohexane–Iso-octane.* For this mixture neither component has appreciable access to the interlamellar pores (see above), and there can be competition for the external surfaces of the crystallites only. For neither component are the partial isotherms independent of varying proportions of the other, and the crystals show no marked preference for either. The isotherms of the two pure hydrocarbons also cross at ~10 cm. pressure. Good separations of this pair would not be possible by adsorption chromatography on the methylammonium clay.

Enrichment Factors

In a sorption equilibrium involving species A and B at mol. fractions N_A^G and N_B^G in the gas phase and N_A^S, N_B^S in the sorbed phase, the enrichment factor for A can be defined as

$$\eta_A = N_A^S N_B^G / N_A^G N_B^S = N_A^S p_B / N_B^S p_A \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p_B and p_A are equilibrium partial pressures in the gas phase. In defining N_A^S and N_B the sorbed phase is regarded as a binary mixture of A and B, just as is the gas phase. A convenient way to express enrichment factors is to plot N_A^S against N_A^G, by analogy with similar diagrams for vapour–liquid mixtures. Fig. 5*a*, *b*, *c*, and *d* show such plots for some of the mixtures which have been studied. A completely non-selective sorption is represented by the diagonal broken lines in the figures. Good enrichments in the intercalated component are seen for each of the three pairs, benzene–cyclohexane, n-heptane–cyclohexane, and hexane–iso-octane, of which the first mentioned component only is intercalated. The more complex behaviour described above, and the change-over in selectivity for the benzene–n-heptane pair are well shown in Fig. 5*a*. Good enrichment factors for either component can occur under appropriately selected conditions.

When, as in the present system, the sorbent provides two distinct sorbing regions, an interlamellar surface and an external surface, there is advantage in considering the selectivities for each region separately:

$$\left.\begin{aligned} \eta_A^i &= \frac{p_B}{p_A} \cdot \frac{N_A^i}{N_B^i} = \frac{p_B}{p_A} \cdot \frac{n_A^i}{n_B^i} \\ \eta_B^a &= \frac{p_B}{p_A} \cdot \frac{N_A^a}{N_B^a} = \frac{p_B}{p_A} \cdot \frac{n_A^a}{n_B^a} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the superscripts " i " and " a " denote " intercalated " and " adsorbed externally " respectively and n's denote actual numbers of moles of A and B intercalated or adsorbed externally. Then for the total numbers of moles of A and B sorbed we have:

$$\left.\begin{aligned} n_A^s &= n_A^i + n_A^a \\ n_B^s &= n_B^i + n_B^a \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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From eqn. 1 we obtain for the measured selectivity:

$$\eta_A = \frac{p_B(n_A^i + n_A^a)}{p_A(n_B^i + n_B^a)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

On rearranging and making use of eqns. 2, we have:

$$n_B^a \eta_A = n_B^i \eta_A^i + n_B^a \eta_A^a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which gives the general relation between the measured enrichment factor, η_A, and those for interlamellar sorption and for adsorption on external surfaces, respectively η_A^i and η_A^a. Eqn. 5 is applicable to the benzene–n-heptane system, after the threshold pressure when intercalation of benzene has commenced.

For the special case when component A is intercalated but not component B, we have $n_B^i = 0$ and, from eqn. 4:

$$\eta_A = \eta_A^a\left(1 + \frac{n_A^i}{n_A^a}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that $\eta_A \longrightarrow \infty$ as required, when $n_A^i/n_A^a \longrightarrow \infty$. Eqn. 6 is then appropriate for n-heptane–cyclohexane, benzene–cyclohexane, and hexane–iso-octane mixtures, and also for the molecular-sieve zeolites. Thus, for chabazite or Linde sieve 5A, the component A could be a n-alkane, and B could be an isoalkane, naphthene, or aromatic hydrocarbon. For these and other zeolites the external surface is very small compared with the internal surface so that n_A^i/n_A^a is very large indeed. The porous clay sorbent considered here differs, for the three mixtures referred to, only in that the ratio of internal to external surface is smaller. This difference arises on account of the small size of clay crystallites. The best molecular-sieve alkylammonium montmorillonites or bentonites will be those having the best developed crystallites, and so the smallest external area. The external areas can be estimated from those of the original Na- or Ca-clay before ion-exchange, or by the method of Barrer and Reay.[3]

When the enrichment factor for n-hexane in admixture with iso-octane is plotted as a function of the partial pressure of n-hexane, it is seen (Fig. 6) that at a given partial pressure of the n-alkane the enrichment factor is *greater* the *poorer* the mixtures are in n-hexane. This situation is the converse of that normally observed when tetramethylammonium montmorillonite is the sorbent (Part II, following paper), but is understandable in terms of eqn. 6. Thus, at fixed partial pressure of A, n_A^i can, if anything, only decrease as the mixture is made richer in B. However, Fig. 4*d* shows that for the mixtures in question n_A^i is virtually unchanged. Consequently the term $(1 + n_A^i/n_A^a)$ increases. η_A^a may, of course, increase or decrease, but the over-all effect can easily be an increase in η_A as the mixtures become poorer in A.

Appendix. Catalytic Activity of Methylammonium Clay.

In several clay–sorbate systems evidence has now been obtained of irreversible sorption processes and of catalytic activity, which may greatly modify their molecular-sieve activity and selectivity. Thus, pyridine could not be desorbed completely from a natural montmorillonite [16,19] or from tetramethylammonium montmorillonite.[14] t-Butyl alcohol was reversibly sorbed by the tetramethylammonium clay,[1] but it was in part dehydrated and the isobutene was polymerised by the monomethylammonium clay.[3] There was also some evidence of dehydration of cyclohexanol by tetramethylammonium montmorillonite.[4] There appears to be no report of sorption of alkenes or alkynes by montmorillonite or its derivatives, and in connection with the mixture isotherms examined in this paper the behaviour of cyclohexene, as an intermediate between benzene and cyclohexane, had been examined.

It was soon apparent that in the monomethylammonium clay irreversible sorption occurred (Fig. 7), although sorption by the tetramethylammonium clay was reversible (see Part II).

[18] Barrer and Robins, *Trans. Faraday Soc.*, 1953, **49**, 929.
[19] Greene-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 425.

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The cyclohexene could not be desorbed, about 5 cm.^{3} at s.t.p. per g. of " cyclohexene " remaining after outgassing. A second isotherm now lay below the first and diverged from it (Fig. 7), and two desorption points showed negligible hysteresis. The results are compatible with polymerisation of cyclohexene to a non-volatile substance which remained trapped in or on the clay crystallites. This polymerised material then acts as a high-boiling liquid and dissolves some cyclohexene, to give the linear second isotherm. After outgassing at 100° the clay gave a *c*-spacing of 11·7 Å, equal to that of the outgassed parent material. A fresh sample of the sorbent saturated with cyclohexene gave a *c*-spacing of ~14·4 Å.

In a further experiment 3 g. of the sorbent, outgassed at 80° for 24 hr., were heated in a sealed tube with excess of cyclohexene at 80°. After removal of the cyclohexene the clay was dark grey-green, but after outgassing the *c*-spacing was 11·6 Å, a figure which rose to ~15 Å at saturation with benzene. A sample of the clay, treated as above with cyclohexene, was extracted in a Soxhlet apparatus with hot benzene; the original colour of the clay was thereby

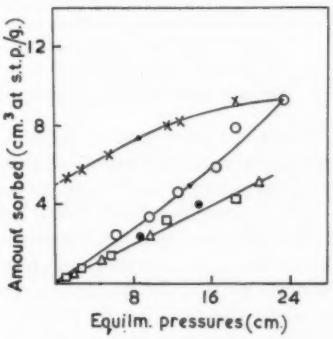

FIG. 7. *Irreversible sorption of cyclohexene at* 80°. *Run* 1: ○ *Adsorption*; × *desorption*. *Run* 2: △ *Adsorption*; ● *desorption*. □ *Calc. desorption*.

restored. Evaporation of the extract gave a small amount of an oil, the infrared spectrum of which did not contain the 3000 cm.$^{-1}$ band of the original cyclohexene. A test for nitrogen was negative. Samples of clay subjected to the action of cyclohexene were then analysed for carbon and hydrogen, with the results shown in Table 3.

TABLE 3.

Treatment of methylammonium clay	Found (%) C	Found (%) H †	Compn. (% by wt.) of sorbed organic material * C	Compn. (% by wt.) of sorbed organic material * H
Specimen A	1·12	1·73	—	—
Specimen B [7]	1·04	1·60	—	—
Sample of A after treatment with cyclohexene (2 days at 80°)	6·40	2·13	93	7
Same sample of A after benzene-extraction	2·03	1·87	86	14
Sample of A used in sorption measurements after outgassing	3·08	1·83	95	5
Pure cyclohexene	—	—	90	10

* *I.e.*, excluding methylammonium ions.
† The figure for H includes any hydrogen present as sorbed H_2O or as OH.

The figures given in the last two columns of Table 3 give, as averages C 91% and H 9%, which are fairly close to the composition of cyclohexene or its polymers. This molecule is known to undergo thermal decomposition, dehydrogenation, and polymerisation.[20] Polymers ranging from dimer to heptamer have been prepared by the action of hydrogen fluoride on cyclohexene.[21] The polymerisation by the clay may be associated with the hydrogen atoms attached to nitrogen in the $Me{\cdot}NH_3^+$ ions, since the tetramethylammonium clay was not catalytically active under our conditions.

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[*Received, July 13th*, 1960.]

[20] Rodd, " Chemistry of Carbon Compounds," Vol. IIA, Elsevier Publ. Co., Amsterdam, 1953.
[21] McElvain and Langston, *J. Amer. Chem. Soc.*, 1944, **66**, 1759.

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180. *Sorption of Mixtures, and Selectivity in Alkylammonium Montmorillonites. Part II.*[1] *Tetramethylammonium Montmorillonite.*

By R. M. Barrer and G. S. Perry.

The sorption of various mixtures of pairs of hydrocarbons of different structural types has been examined in tetramethylammonium montmorillonite. Selectivities vary with the total amount sorbed, the composition of the feed mixtures, and the temperature, and for hydrocarbon pairs of appropriate type can become very large. The affinity decreases in the sequence benzene > n-heptane, n-hexane > cyclohexane > iso-octane. The influence has been studied of varying amounts of these hydrocarbons upon the *c*-spacing of the clay. All the hydrocarbons are intercalated, and in order to explain the selectivities, sorption capacities of the clay and orientations of interlamellar sorbate, not only the intersheet spacing and molecular configuration, but also the distances between the interlamellar organic ions must be taken into account.

Two previous investigations have been made of the intercalation of single sorbates by tetramethylammonium montmorillonite. They have indicated that this sorbent exhibits pronounced selectivities,[2,3] and in consequence excellent separations of various mixtures of organic molecules have been demonstrated.[4] In the present research sorption of mixtures has been investigated to correlate the separations with equilibrium studies, and to determine and interpret selectivities. Steric factors involving interlayer separation in the sorbent, and molecular size and configuration in the sorbate, play important rôles in the ability of the clay to occlude various species. A comparison of these with corresponding factors observed in Part I [1] for monomethylammonium montmorillonite is of particular interest. In the latter sorbent true molecular sieve separations were observed for several categories of mixture, the differences in selectivity depending upon the exclusion of one component from the interlamellar pore space of the sorbent.

Experimental.—The apparatus, sorbates, and *X*-ray procedures have been described in Part I.[1] The tetramethylammonium montmorillonite was taken from a sample previously employed.[4] The parent clay was a Wyoming bentonite.

Results and Discussion

c-Spacings.—The basal spacing of outgassed NMe_4^+-montmorillonite was 13·6 Å, increasing to 13·9 Å in the presence of saturated water vapour, corresponding to intersheet distances of 4·2 and 4·5 Å, respectively. Figs. 1*a* and *b* give the *c*-spacings for the clay crystals equilibrated at various relative pressures and amounts sorbed, for benzene, cyclohexane, n-heptane, iso-octane, and n-perfluoroheptane.

Benzene expands the *c*-spacing to 14·6 Å even at relative pressures as low as 0·05, the spacing being thereafter unchanged up to saturation.[3] There is no evidence that a threshold pressure must be exceeded before penetration occurs, as was the case with $CH_3{\cdot}NH_3^+$-montmorillonite (Part I). Once penetration occurs the spacing for the monomethylammonium clay approaches, with increasing sorption, the slightly larger spacing of 15·0 Å. The intersheet distances in the two sorbents are thus 5·2 and 5·6 Å, respectively, and in both sorbents are considered to be associated with vertically oriented benzene monolayers between the aluminosilicate layers.[3] The intersheet distance reflects the

[1] Part I, Barrer and Perry, preceding paper.
[2] Barrer and MacLeod, *Trans. Faraday Soc.*, 1955, **51**, 1290.
[3] Barrer and Reay, *Trans. Faraday Soc.*, 1957, **53**, 1253.
[4] Barrer and Hampton, *Trans. Faraday Soc.*, 1957, **53**, 1462.

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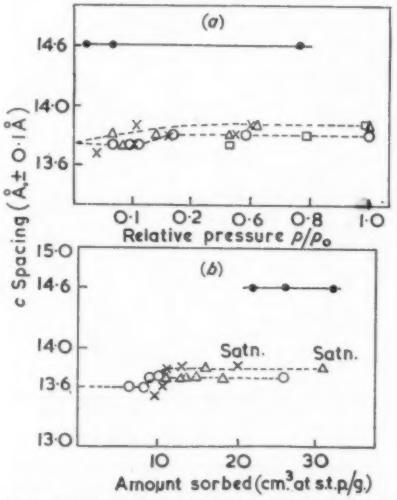
apparent contraction in over-all van der Waals dimensions of intercalated molecules,[3,5-7] associated with keying of atoms of the molecule into the rather open hexagonal networks of the aluminosilicate sheets, or with some compression of the sorbed molecules[3] (see also below).

n-Heptane expands the *c*-spacing of tetramethylammonium montmorillonite from 13·6 to 13·8 Å, the intersheet distance then being 4·4 Å. This contrasts with the behaviour of the monomethylammonium clay, which expanded only to 13·0 Å (Part I), the intersheet distance being 3·6 Å. Two inter-lamellar arrangements of n-alkane chains are possible, which are shown schematically in Figs. 2*a* and *b*. In the first the zig-zag of the n-alkane chain lies parallel to the aluminosilicate layers, the chain thickness normal to the plane of the zig-zag being ~4·0 Å.[8] In the second arrangement this zig-zag lies in a plane normal to the lamellæ, and the chain thickness is 4·9 Å (Figs. 2*b* and *c*). These two orientations

FIG. 1.

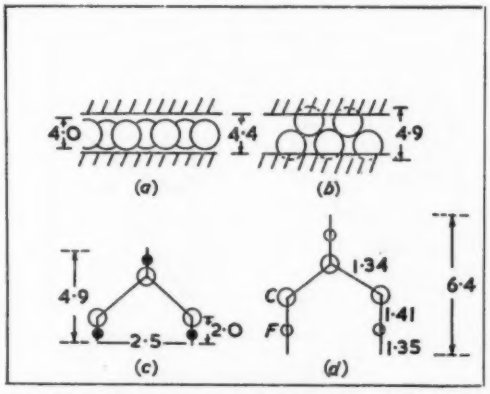


(*a*) c-*Spacings at room temperature for sorbates at various equilibrium relative pressures.*

(*b*) c-*Spacings at room temperature for sorbates as functions of amounts sorbed.*

● *Benzene*; ○ *iso-octane*; × *heptane*; △ *cyclohexane*; □ *perfluoroheptane.*

FIG. 2.



(*a*) *and* (*b*) *The flat and vertical orientations of the zig-zag of n-alkane chains in relation to the free distance between sheets in* NMe_4*-montmorillonite.*

(*c*) *and* (*d*) *Dimensions of the zig-zag in a n-alkane and a n-perfluorocarbon respectively.*

are compatible with the spacings found in the monomethylammonium and tetramethylammonium forms of the clay respectively. The contractions from 4·0 to 3·6 Å and from 4·9 to 4·4 Å in the two sorbents are in line with the apparent contractions in van der Waals dimensions referred to.

The minimum height of the tetramethylammonium ion is 4·9 Å, and the actual intersheet distance in the corresponding ion-exchanged clay (13·6 Å) gives 4·2 Å as intersheet distance, the contraction due to keying of hydrogen atoms into the aluminosilicate sheets or to compression being then 0·7 Å. The chair model of cyclohexane also has a minimum height of 4·9 Å, while that of iso-octane (2,2,4-trimethylpentane) is 5·0 Å. Accordingly, both these sorbates might be expected to produce little expansion when intercalated by

[5] Bradley, *J. Amer. Chem. Soc.*, 1945, **67**, 975.
[6] Greene-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 412.
[7] Talibudeen, *Trans. Faraday Soc.*, 1955, **51**, 582.
[8] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1941, p. 189.

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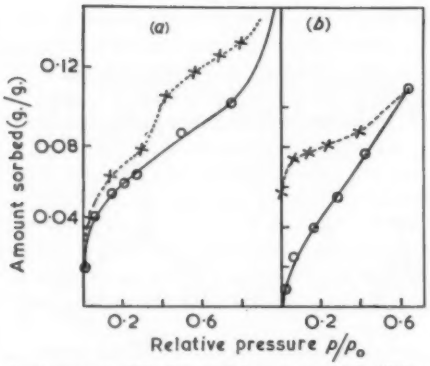
the tetramethylammonium clay. Indeed, Figs. 1*a* and *b* show that this is the case, the expansion being if anything less than for n-heptane. The thickness of the cyclohexene molecule is ~4·6 Å, and it was also observed that a sample of the clay saturated with this sorbate gave *c*-spacings of 13·7 Å, the intersheet distance being ~4·3 Å. This small expansion, together with the substantial sorption (Fig. 3*a*), is evidence of penetration between the aluminosilicate layers. Like benzene, other hydrocarbons such as n-heptane and cyclohexane give, on the above evidence, variously oriented monolayers within the clay, and in admixture with the organic ions.

n-Perfluoroheptane was the only one of the sorbates investigated here which failed to penetrate. The height of the zig-zag of the n-perfluoroheptane chain in the interlamellar orientation of Fig. 2*b* would be 6·4 Å (Fig. 2*d*). In the orientation of Fig. 2*a* this height

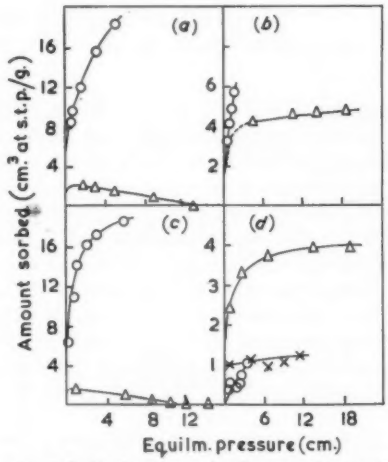
FIG. 3.



Isotherms at 60° for cyclohexene on (a) NMe_4-montmorillonite and (b) the parent Ca-clay from which the alkylammonium clay was prepared.

○ = *Adsorption*, × = *desorption.*

FIG. 4.



(*a*) *and* (*b*) *Isotherms for benzene* (○) *and heptane* (△) *from two mixtures*; (*a*) 0·67, (*b*) 0·30 *mol. fraction of benzene.*

(*c*) *Isotherms for benzene* (○) *and cyclohexane* (△) *from a mixture*; 0·67 *mol. fraction of benzene.*

(*d*) *Cyclohexane isotherms from several mixtures with n-heptane*; *mol. fraction of n-heptane*: ○ 0·85, × 0·56, △ 0·16.

(*All isotherms refer to* 80°.)

would be 5·5 Å. In long-chain n-perfluorocarbons, however, the simple zig-zag may, for steric reasons, be replaced by a helix which could have a considerable diameter [9] (~5·9 Å). In any case a substantial expansion of the clay would be necessary if intercalation occurred, which is certainly not observed (Fig. 1*a*). This, coupled with the small sorption (Table 1), indicates negligible interlamellar penetration. Some of this sorption may be due to impurities in the n-perfluoroheptane, accounting for the slight expansion at high relative pressures.

Isotherms of Single Sorbates.—The isotherms of most single sorbates may be considered, when necessary, in connection with the isotherms of their binary mixtures (see below). The B.E.T. monolayer equivalents, v_m, are summarised in Table 1 as obtained in the

[9] Bunn, *Nature*, 1954, **174**, 549.

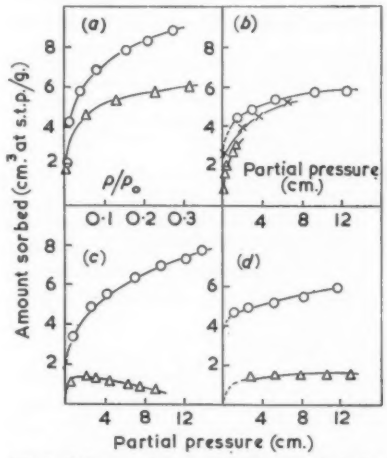
TABLE 1. *Monolayer equivalents (cm.³ at s.t.p./g. outgassed weight).*

Sorbate	v_m values: This work	v_m values: Ref. 10	Area of sorbate molecule * (Å²)	Equiv. monolayer area (m.²/g.) (this work)
Benzene	21·2	25·0	25	143
Cyclohexane	6·8	11·3 [11]	46	84
Cyclohexene	7·7	—	43	89
n-Heptane	6·4	9·2	51	88
n-Hexane	6·7	—	44	79
Iso-octane	4·7	6·9	52	65
n-Perfluoroheptane	2·6	—	78 †	54

* Estimated from Courtauld models. † Calc. for zig-zag chain form.

present and in earlier work.[10,11] The B.E.T. method, for sorption which is partly interlamellar and partly associated with uptake upon external surfaces, has substantial limitations,[3] and the molecular areas are also approximate. The most accurate v_m value and equivalent monolayer area are those for benzene, but the above uncertainties make the actual isotherms the best measure of the considerable capacity of the sorbent.

FIG. 5.



(*a*) *Cyclohexane* (○) *and n-heptane* (△) *isotherms for each pure sorbate.*

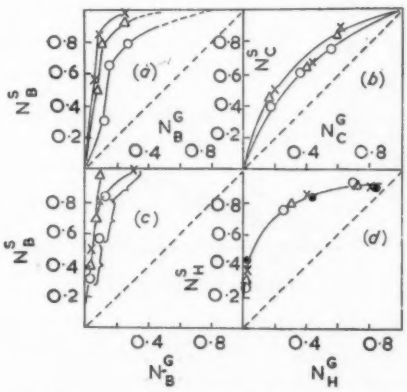
(*b*) *n-Heptane isotherms from several mixtures with cyclohexane; mol. fractions of n-heptane:* ○ 0·85, × 0·56, △ 0·16.

(*c*) *Isotherms for cyclohexane* (○) *and iso-octane* (△) *in a mixture; 0·70 mol. fraction of cyclohexane.*

(*d*) *Isotherms for n-hexane* (○) *and iso-octane* (△) *in a mixture; 0·55 mol. fraction of hexane.*

(*All isotherms refer to* 80°.)

FIG. 6. *Equilibrium composition diagrams for 80° at various total pressures for (a) benzene in mixtures with n-heptane, (b) cyclohexane in mixtures with iso-octane, (c) benzene in mixtures with cyclohexane, and (d) heptane in mixtures with cyclohexane.*



Total pressures (cm.): (*a*) ○ 2·5, △ 10·0, × 15·0; (*b*) ○ 2·5, △ 10·0, × 20·0; (*c*) ○ 2·5, △ 10, × 20; (*d*) ○ 2·5, △ 5·0, × 10·0, ● 20·0.

For individual points on the curves, mol. fractions of the first-named constituents in the initial mixtures were, reading upwards: (*a*) 0·30, 0·50, 0·67; (*b*) 0·30, 0·52, 0·70; (*c*; *in triads*) 0·16, 0·47, 0·67; (*d*; *in groups of four*) 0·16, 0·56, 0·85.

The uptake of cyclohexene (Fig. 3*a*) was free from the chemical side-reaction noted with the methylammonium clay, but was associated with an extended hysteresis involving lattice expansion. The isotherm is closer to that of cyclohexane than of benzene. The sample of tetramethylammonium montmorillonite was prepared from a Ca-montmorillonite * having a substantially larger external surface area than the Wyoming bentonite

* Kindly supplied by Fuller's Earth Union, Redhill.

[10] MacLeod, Ph.D. Thesis, Aberdeen, 1955.
[11] Reay, Ph.D. Thesis, London, 1956.

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used as parent material for all other alkylammonium clays of this paper and of Part I. An augmented uptake of cyclohexene gave an equivalent monolayer area of ~205 m.²/g. The parent clay gave the unusual isotherm of Fig. 3*b*, where however a chemical reaction may be occurring (cf. Part I). v_m for cyclohexene in Table 1 refers to an isotherm at 80° on NMe_4-montmorillonite derived from the Wyoming bentonite, and by which cyclohexene was less copiously sorbed.

Mixture Isotherms.—Isotherms of mixtures were measured at 80° c over a range of compositions for the following systems: Benzene–n-heptane (0·67, 0·50, 0·30), benzene–cyclohexane (0·67, 0·47, 0·24), n-heptane–cyclohexane (0·85, 0·56, 0·16), cyclohexane–iso-octane (0·70, 0·52, 0·30), n-hexane–iso-octane (0·70, 0·55, 0·23). The figures in parentheses refer to the constant mol. fraction of the first-mentioned component in the feed mixture. In addition, the benzene–n-heptane mixture having a mol. fraction of benzene of 0·67 was studied at 85°, 90°, and 95°. In Figs. 4 and 5 are presented some of the partial isotherms obtained at 80°.

(a) *Benzene–n-heptane.* Benzene is selectively sorbed for all the compositions of feed mixtures studied, and as the sorption of benzene increases, n-heptane is progressively

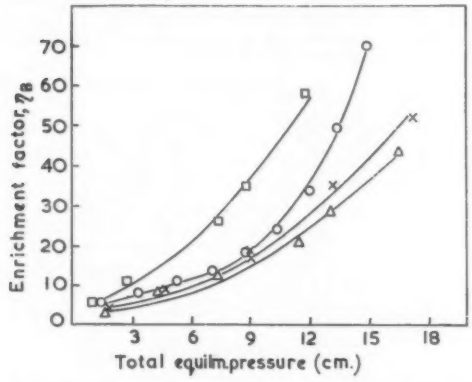

FIG. 7. *Enrichment factors as functions of pressure and temperature for benzene in a benzene–n-heptane mixture.*
□, 80°; ○ 85°; × 90; △ 95° c.

displaced from the sorbent, until a position is reached in certain mixtures in which the sorbed phase is virtually pure benzene (*e.g.*, Fig. 4*a*). Similar but less complete displacements have also been reported for binary mixtures of permanent and noble gases occluded by zeolites.[12] In tetramethylammonium montmorillonite the enrichment factor can be extremely large under certain conditions. There is no evidence of the formation of the "adsorption azeotrope" observed for this mixture in the monomethylammonium clay (Part I), in comparison with which the selectivity towards benzene is much enhanced.

(b) *Benzene–cyclohexane.* This pair behaves very similarly to the benzene–n-heptane mixtures, the cyclohexane being, under appropriate conditions and for appropriate compositions, completely displaced from the sorbent (Fig. 4*c*), so that then the enrichment factor for benzene becomes as before indefinitely large. High selectivities to benzene were observed also with the monomethylammonium clay (Part I).

(c) *n-Heptane–cyclohexane.* The isotherms of the pure single sorbates (Fig. 5*a*) show that more cyclohexane than n-heptane is taken up at a given relative pressure. Nevertheless, the affinity of the n-heptane for the clay is superior to that of cyclohexane, as is demonstrated by the partial isotherms of each species shown in Figs. 4*d* and 5*b*. In competitive sorption, the uptake of n-heptane is affected much less by presence of cyclohexane than conversely, and the adsorbed phase is much enriched in n-heptane. The separation is again in the direction observed for the monomethylammonium clay (Part I).

[11] Barrer and Robins, *Trans. Faraday Soc.*, 1953, **49**, 929.

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(d) *n-Hexane–iso-octane and cyclohexane–iso-octane.* In both these mixtures the first-mentioned component was always selectively sorbed (*e.g.*, Figs. 5*c* and 5*d*). The good separation of hexane from iso-octane [4] is reflected in the enrichment factor, which varied from 9·5 to 4·7 for the feed mixture having a mole fraction of 0·55 of n-hexane.

Selectivity.—The mixture isotherms can be further interpreted in terms of enrichment factors (or selectivity coefficients), η, defined for component A in a mixture of A and B by (Part I):

$$\eta_{A} = \frac{N_A^S}{N_B^S} \cdot \frac{N_A^G}{N_B^G} = \frac{N_A^S}{N_B^S} \cdot \frac{p_A}{p_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N's denote mol. fractions and the superscripts " S " and " G " denote " sorbed phase " and " gas (or vapour) phase " respectively. The enrichments for component A can be usefully presented in the form of curves of N_A^S *vs* N_A^G, as in Fig. 6. In this Figure the subscripts " B," " C," and " H " denote respectively benzene, cyclohexane, and

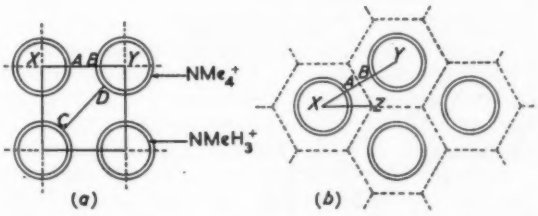

FIG. 8. (*a*) *and* (*b*) *The square and hexagonal arrays of alkylammonium ions considered in relation to inter-ion spacing, showing free distances of importance.*

n-heptane. The results of the preceding section and Fig. 6, and corresponding data for the monomethylammonium clay (Part I), may now be compared. First, in the tetramethylammonium clay the affinity sequence can be written as:

benzene > n-heptane, n-hexane > cyclohexane > iso-octane

which to some extent can no doubt be regarded as representative of the corresponding classes of hydrocarbon. For separations of simple aromatic compounds from n-alkanes this sorbent is to be preferred to the monomethylammonium clay. In separations of aromatic compounds from simple naphthenes both sorbents should be effective, but the tetramethylammonium form can give larger coefficients, η_B, under appropriate conditions. In separations of n-alkanes such as heptane or hexane from simple cycloalkanes both sorbents can be effective and the evidence is that the monomethylammonium clay might be especially good. For separating straight- from branched-chain paraffins (*e.g.*, n-heptane or n-hexane from iso-octane) both sorbents could be effective, but for the cyclohexane–iso-octane pair only the tetramethylammonium clay offers a reasonable enrichment combined with moderate sorptive capacity.

Inspection of Figs. 6 and 7 shows that the enrichment factors can depend strongly on the total pressures, and so on amount sorbed, as well as on the composition of the feed mixture, so that choice of the correct range of physical operating conditions can be important. Enrichments also depend upon temperature, as is shown for benzene–heptane mixtures in Fig. 7. Better enrichments are here clearly obtained at lower temperatures, and also for higher pressures or larger amounts sorbed (excluding the region where capillary condensation in spaces between clay crystallites can occur). The temperature-dependence of the enrichment factors is in accord with the results of other workers,[13,14] and could be anticipated from simple theories of the adsorption process.

Interlamellar Cations.—(a) *Complete ion exchange.* The interplay of steric and other factors determining selective sorption by expanded montmorillonites has been discussed

[13] Reeds and Kammermeyer, *Ind. Eng. Chem.*, 1959, **51**, 1707.
[14] Benedek and Szepesy, *Acta Chim. Acad. Sci. Hungary*, 1958, **14**, 31.

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with considerable success in terms of intersheet spacing and molecular shape and dimensions,[2,3,4,15,16] but less attention has been given to the importance of lateral distances between the organic ions located between the aluminosilicate layers. Thus, for a series of hydrocarbon molecules all of which can penetrate into the interlamellar spaces we have demonstrated that profound differences in selectivity are still found. The question arises as to whether such differences do not originate at least in part from *lateral* interionic spacings.

That ion size can largely determine the interlamellar sorptive capacity of a given expanded clay sorbent has been very well shown in the case of tetramethyl- and tetraethyl-ammonium montmorillonite.[2] The capacity for sorbing benzene is about three times as large for the former as for the latter, although after imbibing this molecule each clay should show practically the same intersheet distance. The more bulky NEt_4^+ ion

FIG. 9*a*. *Possible orientations of non-rotating tetramethylammonium ions in a regular array on the hexagonal oxygen network of the clay, showing resultant variable free distances between ions.*

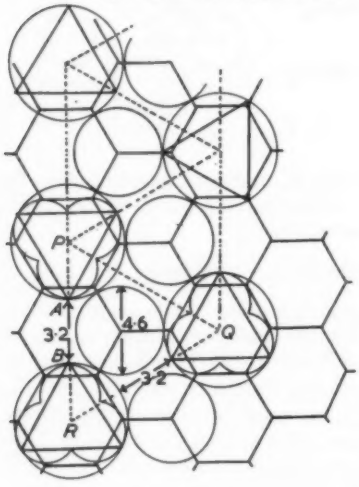
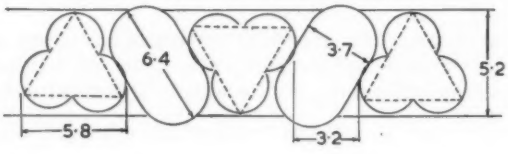


FIG. 9*b*. *Interlamellar orientation suggested for benzene molecules between tetrahedral* NMe_4^+ *ions.*



fills much more of the intersheet pore volume than does the NMe_4^+ ion. Calculations were then made of the extent of the available intersheet areas when organic ions of different dimensions replace completely the small inorganic ions of the parent clay.[3,15] Although this approach gave qualitative agreement with experiment, the observed intersheet areas were normally less than those calculated. We therefore now propose to consider the actual free distances between organic ions in relation to the molecular dimensions of sorbates.

Square and hexagonal arrays of interlamellar cations were considered (Fig. 8). In the square array two free distances AB and CD can be considered, and one distance XY between ionic centres. In the hexagonal array one free distance AB and one distance XY are required. We accept for the calculations Ross and Hendricks's idealised formula[17] for the unit cell content of outgassed montmorillonite: $[Si_8Al_{3\cdot33}Mg_{0\cdot67}O_{20}(OH)_4]M_{0\cdot67}^+$ where M^+ denotes the exchangeable ion and in which the "a" and "b" dimensions of

[15] Barrer and Reay, 2nd Internat. Congress on Surface Activity, Butterworths, London, 1957, p. 79.
[16] Barrer and MacLeod, *Trans. Faraday Soc.*, 1954, **50**, 980.
[17] Ross and Hendricks, U.S. Geol. Survey, Prof. Paper 205B, 1945.

the unit cell are 9·0 and 5·2 Å. In absence of any cations, the surface area per g. unit cell consisting of a single sheet with two surfaces would be 560×10^3 m.^{2}. This area represents only external area. When the crystal is two sheets thick, there are 280×10^3 m.^{2} of external area and 140×10^3 m.^{2} of internal area per g. unit cell, because in general only a monolayer of ions or of sorbate is present between a pair of sheets. Similarly in a pile consisting of n aluminosilicate sheets the internal area is $[(n-1)/2n] \times 560 \times 10^3$ m.^{2}/g.u.c. and the external area is $[2/2n] \times 560 \times 10^3$ m.^{2}/g.u.c. When n is large enough, the internal area is thus 280×10^3 m.^{2}/g.u.c. Such areas are not developed in actual expanded clay crystals because, *inter alia*, part of the intersheet area is occupied by cations.

In a square array, with only the intersheet areas considered, each cation, of which there are $0{\cdot}67 \times 6{\cdot}02 \times 10^{23}$ per g.u.c., is shared with four squares of which therefore there is an equal number each of area $280 \times 10^{23}/0{\cdot}67 \times 6{\cdot}02 \times 10^{23} = 70$ Å^2. Thus the square edge (XY in Fig. 8*a*) is 8·4 Å. Correspondingly in a hexagonal array each cation is shared by six triangles of area 35 Å^2 and edge XY (Fig. 8*b*) of 9·0 Å. The shortened intersheet distances of the alkylammonium montmorillonites as compared with the van der Waals diameters of the ions (this paper and ref. 3) indicate keying of the ions into the six-membered rings of the aluminosilicate sheets. This is not possible for the square array with $XY = 8{\cdot}4$ Å which therefore need not be considered further, but is exactly possible for the hexagonal array with $XY = 9{\cdot}0$ Å, there being one alkylammonium ion above the centre of each alternate hexagon of oxygen atoms of diameter 5·2 Å and free diameter (5·2 − 2 × radius of O) = 2·4 Å (Fig. 9*a*). This free diameter determines the extent of any keying of the organic ions into the oxygen network.

For a hexagonal network of the organic ions NMe_4^+ and NH_3Me^+, rotating about axes normal to the aluminosilicate sheets, Barrer and Reay [3,15] estimated areas of about 26 and 17 Å^2, respectively, corresponding to radii of ~2·9 and 2·4 Å. In the hexagonal array the free inter-ion distances are 3·2 Å for the NMe_4^+-clay and 4·2 Å for the NH_3Me^+-clay, while the corresponding diameters of the largest circles which can be inscribed in the hexagonal array to touch each of three ions are respectively 4·6 and 5·6 Å. If the alkylammonium ions cease to rotate, then according to their mutual orientations towards each other, some or all of the above dimensions will increase to a certain extent. This is shown in Fig. 9*a* for NMe_4^+ ions having their triangular bases parallel to the aluminosilicate sheets. Some of these bases may be adhering to the upper lamella, and some to the lower, and this may further modify the free inter-ion distances. The latter situation does not arise for the dumb-bell-shaped NH_3Me^+ ion. The intersheet distance being only 2·2 A (Part I) these ions probably lie with their long axes parallel with the sheets, with keying of H atoms into upper and lower sheets of anionic oxygens. This is the orientation considered by Barrer and Reay [3] in estimating the area. If the lattice expands sufficiently on intercalating the sorbate (*e.g.*, in presence of benzene) the NH_3Me^+ ions could reorient with their long axes normal to the aluminosilicate sheets, and this would also augment the free inter-ion distances AB. We thus see that the distances given above tend to be lower linits, characteristic only of rotating states of the interlamellar ions.

With this qualification in mind, for hexagonal arrays of rotating ions the following comments may be made:

(i) From the dimensions of benzene considerable compression would be necessary if this molecule were intercalated by either NMe_4^+- or NH_3Me^+-clay with the benzene nucleus parallel to the aluminosilicate sheets. This situation would be eased only in part if rotation of organic ions ceased, because while some of the gaps between ions are rather large some are still small (Fig. 9*a*). On the other hand, with non-rotating ions and the more economical packing associated with vertical orientation of the benzene rings all the interionic space could be available.

With the triangular bases of alternate NMe_4^+ ions adhering respectively to the upper and the lower aluminosilicate sheets, a tilted stacking of benzene molecules is required, as shown in Fig. 9*b*. On the other hand, for NH_3Me^+-montmorillonite the stacking can

be vertical. This observation may reasonably explain the greater intersheet distance (5·6 Å) reached with the $CH_3{\cdot}NH_3^+$-clay than with the NMe_4^+-clay (5·2 Å).

(ii) The intersheet distances for cyclohexane and cyclohexene complexes with NMe_4^+-montmorillonite are too small for vertical orientation of these species, but the molecules have considerable lateral dimensions. It is suggested therefore that these two compounds, and also the bulky iso-octane molecule, occupy only the larger gaps associated with non-rotating states of the tetramethylammonium ions (Fig. 9*a*). In this event the capacity of the sorbent will be much reduced as compared with that for benzene. Comparison of the equivalent monolayer values, v_m, of Table 1, or direct comparison of the sorption isotherms, shows that the predicted difference in capacity exists.

(iii) The intersheet distances of the n-alkane complexes of NH_3Me^+- and NMe_4^+-montmorillonite (Section 3) suggest respectively horizontal and vertical orientations of the plane of the zig-zag of the carbon chain. The greater free distance between NH_3Me^+-ions may be decisive in allowing the horizontal arrangement in the NH_3Me^+-clay.

(b) *Partial ion exchange.* The partial exchange of small Na^+ or Ca^{2+} ions by alkylammonium ions raises interesting but so far unexplored problems. The small inorganic ions can be sunk into the six-membered rings of the aluminosilicate sheets.[18] They may therefore play little part in excluding sorbate molecules from the dehydrated crystals, and are partly screened by ambient negatively charged oxygen atoms. If the large organic ions are located over the remainder of the sites in the hexagonal array of Fig. 9*a*, this array will have a statistically distributed series of gaps, and the average distance between nearest neighbour pairs of organic ions must increase as the amount of exchange decreases and with it the available intersheet porosity and monolayer equivalent areas must rise. It should indeed be possible to approach more nearly the maximum interlamellar sorptive capacity of the clay of 280×10^3 m.^{2}/g.u.c. Some average free inter-ion distances (*AB* of Fig. 8*b*) are given in Table 2.

TABLE 2. *Average free distances* AB (*Fig.* 8) *between organic ions in partially ion-exchanged montmorillonites.*

Ions in hexagonal array	Average free distances in Å for % exchange				
	100	80	60	40	20
NMe_4^+	3·2	4·4	5·9	8·4	14·3
NH_3Me^+	4·2	5·4	6·9	9·4	15·3

Conclusion.—The considerations of the previous section indicate that distributions and orientations of, and distances between, the organic interlamellar cations introduce steric factors into the sorption phenomena comparable in importance with intersheet distances and molecular configuration in determining the sorption capacities and strong selectivities shown by expanded clay sorbents. Only by considering all three factors together can one attempt to interpret the selectivity, or the orientation of the interlamellar monolayers of sorbate. No quantitative theory of the observed enrichment factors is possible, because the sorption equilibria do not follow any simple isotherm equation, and because both interlamellar and external surfaces of the crystallites are simultaneously involved and may vary in proportions between specimens. Nevertheless, it has been possible to measure enrichment factors quantitatively and to demonstrate the way in which they depend upon amount sorbed, composition of feed material, and temperature. In utilising to the best advantage the selectivity of expanded clay sorbents as separation media, reliable information of this kind must be obtained and interpreted.

One of us (G. S. P.) gratefully acknowledges the award of a scholarship by the Fuller's Earth Union Ltd., Redhill, which enabled him to participate in the work described in this and the preceding paper.

IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, July 13th,* 1960.]

[18] Barrer and Reay, *J.*, 1958, 3824.

181. *Studies of Aromaticity by Nuclear Magnetic Resonance Spectroscopy. Part I. 2-Pyridones and Related Systems.*

By J. A. Elvidge and L. M. Jackman.

Proton chemical shift data have been used in three ways to estimate the aromatic character of the 2-pyridone ring. The results are reasonably consistent and indicate that 2-pyridones have *ca.* 35% of the aromaticity of benzene, as defined by ability to sustain an induced ring current. The formally related 1,2-dihydro-2-methylenepyridine system is not aromatic: this conclusion has bearing on the constitution of adducts from pyridine and 3-picoline with acetylenedicarboxylic ester.

One of the best understood mechanisms for proton magnetic shielding is that arising from induced circulations of π-electrons in benzenoid aromatic systems.[1-4] These induced circulations (or ring currents) are responsible for the shielding of protons attached to aromatic rings,[2,3,4] for the paramagnetic shift observed for the protons of a methyl substituent,[3] as in toluene, and for the diamagnetic shielding of the central methylene protons in *p*-polymethylenebenzenes.[4] Calculated magnitudes of these effects agree satisfactorily with the experimental values. Thus there are reliable means of estimating the magnitude of the ring current induced in a closed conjugated system.

Textbooks do not in general attempt succinct definitions of the term "aromatic compound."[5] It is usual to direct attention to the characteristic properties. It emerges that an aromatic compound is always a mono- or poly-cyclic conjugated or cross-conjugated system, but such a system is not of necessity aromatic. The essential feature is a ring of atoms so linked that π-electrons are delocalised right round the ring. *We can define an aromatic compound, therefore, as a compound which will sustain an induced ring current.* The magnitude of the ring current will be a function of the delocalisation of π-electrons around the ring and therefore a measure of aromaticity. Our treatment is confined initially to six-membered monocyclic systems as these can be compared directly with benzene, in which there is full delocalisation of the π-electrons as indicated by the D_{6h} symmetry. Additional computation will be required for the treatment of other than six-membered rings and for fused aromatic ring systems.

Aromatic character in many heterocyclic and in non-benzenoid aromatic compounds is certainly less well defined than for benzenoid hydrocarbons because the usual chemical criteria are essentially qualitative and frequently ambiguous. In principle it is possible to express the aromatic character of all types of system quantitatively in terms of resonance energy, but experimentally it is difficult to obtain meaningful values for borderline, weakly aromatic systems. Arguments based on proton chemical shifts are likely to prove much more definitive and may lead to a quantitative assessment of aromaticity for all types of cyclic system.

We have begun a study of chemically less-defined aromatic systems and herein describe attempts to characterise the aromaticity of 2-pyridones. We conclude that these compounds have only 35% of the aromaticity of benzene.

In order to obtain suitable chemical-shift data for the discussion of aromatic character in the 2-pyridone system, we have determined the line positions (τ values) for protons

[1] Pople, *J. Chem. Phys.*, 1956, **24**, 1111.
[2] Bernstein, Schneider, and Pople, *Proc. Roy. Soc.*, 1956, *A*, **236**, 515; Pople, *Mol. Phys.*, 1958, **1**, 175; McWeeny, *ibid.*, p. 311.
[3] Johnson and Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
[4] Waugh and Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846.
[5] See, *e.g.*, Cram and Hammond, "Organic Chemistry," McGraw-Hill Book Co. Inc., New York, 1959; Finar, "Organic Chemistry," 3rd edn., Longmans, Green and Co., London, 1959, Vol. I; de la Mare and Ridd, "Aromatic Substitution," Butterworths, London, 1959; Hückel, "Theoretical Principles of Organic Chemistry," Elsevier, Amsterdam, 1955, Vol. I; Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

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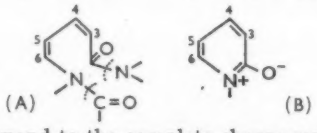
attached directly to the ring and for the protons of substituent methyl groups. From the results, given in Table 1, the shielding contributions arising from a ring current can be assessed provided the line positions in the absence of a ring current can be predicted. This becomes possible from consideration of model structures in which the π-electrons are regarded as rigidly localised. An alternative approach is given below.

TABLE 1. *Chemical shift data (at 21° in* $CDCl_3$).

		τ values for ring and subst. group protons at position				
No.	2-Pyridones	3	4	5	6(2)	1
1	1-Me	3·43	2·74	3·85	2·69	6·41
2	1,3-Me_2	7·85	2·88	3·93	2·75	6·47
3	1,5- ,,	3·49	2·80	7·92	2·89	6·48
4	1,6- ,,	3·56	2·78	3·96	7·64	6·46
5	1,4,6-Me_3	3·74	7·90	4·09	7·68	6·49
6	3-Ac-5-EtO_2C-1,4,6-Me_3	7·48(Ac)	7·88	5·68(CH_2) 8·63(Me)	7·62	6·45
	Pyridines					
7	(Pyridine [a])	3·01	2·64	3·01	1·50	
8	2,4-Me_2	3·17	7·74	3·14	7·56 1·77	
9	2,6- ,,	3·07	2·45	3·07	7·48	
10	3,5- ,,	7·74	2·83	7·74	1·88	
11	3,5-(EtO_2C)$_2$-2,6-Me_2	5·61(CH_2) 8·58(Me)	1·48	5·61 8·58	7·22	
12	3,5-(EtO_2C)$_2$-2,4,6-Me_3	5·56(CH_2) 8·61(Me)	7·70	5·56 8·61	7·45	
	Pyridinium iodides					
13	2,6-Me_2-1-Et	2·06	1·59	2·06	6·95	5·26(CH_2) 8·42(Me)
14	2,4-Me_2-1-Et	2·15	7·35	2·15	7·03 0·74	5·15(CH_2) 8·35(Me)
15	1,2,4-Me_3 [b]		7·42		7·06	
16	1,3,5-Me_3	7·40	1·88	7·40	0·94	5·41
17	3,5-(EtO_2C)$_2$-1,2,4,6-Me_4 [c]	5·51(CH_2) 8·58(Me)	7·56	5·51 8·58	7·14	5·69
	Miscellaneous					
18	Et_2 1,2-dihydro-2-methylene-1,4,6-trimethylpyridine-3,5-dicarboxylate		8·13		7·81(Me) 6·45(CH_2)	6·96
19	Me sorbate				8·13	

[a] Ref. 8, p. 64. [b] The formation of a two-phase system in $CDCl_3$ resulted in serious loss of resolution. [c] Examined as the methosulphate (Me, 6·45).

For 2-pyridone (I), two extreme *non-aromatic* models are (A) and (B),* the latter being the better if aromatic character is fully developed in the 2-pyridone system. We suspect that this zwitterion model (B) is only a partial approximation to a true non-aromatic model because the dipole moment of 1-methyl-2-pyridone, though large (4·15 D



in benzene [6]), does not correspond to the complete charge separation in (B) which may be compared with that [7] in glycine zwitterion (15 D). The two models differ appreciably in inductive and mesomeric contributions to the local diamagnetic shielding of the relevant protons. Such effects are particularly serious when ring protons are considered [8] and

* It is emphasised that (A) and (B) are fixed-bond model structures. Thus (B) is a non-resonating aza-cyclohexatriene, and is not meant to represent a hybrid structure.

[6] Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, p. 355.
[7] Ref. 6, p. 354.
[8] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 63.

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for this reason we have made use first of the shifts for methyl-protons as these are relatively unaffected. Thus a *m*- or a *p*-nitro-substituent causes a paramagnetic shift of only 0·09 p.p.m. for the methyl protons of toluene.[9] A disadvantage is that the shifts observed for methyl-protons are smaller for a given ring-current density than for ring protons.

Model (A) is not available but the resonance frequencies of protons on methyl substituents at the four positions can be reliably predicted because the major shielding effects will be associated with the magnetic anisotropies of the various multiple bonds. A methyl group at the 3-position has an environment similar to that experienced by an α-methyl group in a carotenoid monoester (*e.g.*, compound 38 in ref. 10) and should absorb at τ 8·06 (in $CDCl_3$). The corresponding amide is not available but the value would be virtually the same (cf. methacrylic ester 8·10 ± 0·02 and methacrylamide [11] 8·06 ± 0·02) and there is little difference from the corresponding aldehydes,[10] which shows that the polarity of the carbonyl group is unimportant. For a 4-methyl group we predict τ 8·01 by subtracting 0·15 (the frequency difference between " in-chain " and " end-of-chain " methyl-protons in carotenoid esters [10]) from the value (8·16) for the methyl (protons) *trans* to carbonyl in methyl senecioate.[11] A 5-methyl group approximates to the " in-chain " methyl groups of a carotenoid or carotenoid ester (compounds 3, 11, 12, 17, and 25 in ref. 10) and should absorb at 8·03 (for $CDCl_3$ solution). A methyl group at the 6-position is at the end of the conjugated carbon chain and should absorb as in sorbic ester (8·13) (Table 1) except that it will experience a further paramagnetic shift of 0·1 p.p.m. because of the neighbouring nitrogen atom: [12] hence the predicted value for the 6-methyl group protons is 8·03.

In model (B) any *C*-methyl substituent corresponds to an " in-chain " methyl group in carotenoids (8·03), except that when attached at the 6-position it is close to the positive pole on nitrogen and so a paramagnetic correction of 0·63 is required here. The correction comprises 0·1 p.p.m. for the inductive effect of the nitrogen atom and 0·53 p.p.m. for the positive pole, the latter value being the shift for the α-methyl groups in the pyridine (no. 9 of Table 1) which results on quaternisation to compound (13).

TABLE 2. *Proton resonance values* ($\tau_{obs.}$) *for C-methyl substituents of* 1*-methyl-2-pyridones compared with values* ($\tau_{calc.}$) *for the non-aromatic models* (A) *and* (B).

		Model (A)		Model (B)	
Me position	$\tau_{obs.}$	$\tau_{calc.}$	$\tau_{calc.} - \tau_{obs.}$	$\tau_{calc.}$	$\tau_{calc.} - \tau_{obs.}$
3	7·85	8·06	0·21	8·03	0·18
4	7·89 [a]	8·01	0·12	8·03	0·14
5	7·92	8·03	0·11	8·03	0·11
6	7·65 [b]	8·03	0·38	7·40	−0·26

Average of values (*a*) for compounds (5) and (6) and (*b*) for (4), (5), and (6) in Table 1.

Table 2 allows comparison of these predicted values with the experimental results. The models (A) and (B) give reasonable agreement for ($\tau_{calc.} - \tau_{obs.}$) for all positions of the methyl substituent except the 6-position. This is expected because this position is most affected by the development of the zwitterion on passing from model (A) to (B). It might be argued that the 6-methyl group could seriously distort the planarity of the sp^2-hybridised nitrogen atom. That this is not so is shown by the narrow range of absorption of the *N*-methyl group protons (6·41—6·49) in the various 2-pyridones (Table 1).

The average shift ($\tau_{calc.} - \tau_{obs.}$) in Table 2, derived from both models, with neglect of values for the 6-position, is 0·14(5) p.p.m. Because the ring-current contribution to the shielding of the methyl group protons in toluene is 0·40 p.p.m. [being the difference in line position (τ 7·66) from that of an " in-chain " methyl group in a carotenoid (8·06)], it

[9] Ref. 8, p. 58.
[10] Barber, Davis, Jackman, and Weedon, *J.*, 1960, 2870.
[11] Jackman and Wiley, *J.*, 1960, 2881.
[12] Ref. 8, p. 53.

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follows that the 2-pyridone ring sustains only 36% of the induced ring current of benzene and so has a fractional aromaticity of 0·36.

An alternative method of assessing the ring current involves starting with fully aromatic models and predicting empirically the line positions in the absence of a ring current. To do this we start with the corresponding alkylated pyridines as being related to model (A) and their quaternary salts as being similarly related to (B). It is then assumed that the ring currents in these two systems make the same contribution, 0·4 p.p.m., to the shielding of methyl substituents as does the ring current in toluene. (There is little doubt that pyridine is as fully aromatic as benzene [13].) Data for the appropriate methylpyridines and their quaternary salts, included in Table 1, then allow the computation of the $\tau_{calc.}$ values listed in Table 3.

The data (in Table 3) derived from the non-aromatic pyridine model overestimate the ring-current contribution ($\tau_{calc.} - \tau_{obs.}$) whereas those derived with the non-aromatic

TABLE 3. *Comparison of proton resonance values* ($\tau_{obs.}$)[a] *for* C-*methyl substituents of* 1-*methyl*-2-*pyridones with values* ($\tau_{calc.}$) *for the non-aromatic pyridine and pyridinium models.*

	Non-aromatic pyridine model		Non-aromatic pyridinium model	
Me position	$\tau_{calc.}$	$\tau_{calc.} - \tau_{obs.}$	$\tau_{calc.}$	$\tau_{calc.} - \tau_{obs.}$
3	8·14[b]	0·29	7·80	−0·05
4	8·12[c]	0·23	7·84[e]	−0·05
5	8·14	0·22	7·80	−0·12
6	7·83[d]	0·18	7·44	−0·21

(*a*) As in Table 2. (*b*) Value for compound (10) of Table 1, 7·74, plus 0·4. (*c*) Similarly from average values for (8) and (12). (*d*) for (8), (9), (11), and (12), (*e*) for (14), (15), and (17), and (*f*) for (13), (14), (15), and (17) in Table 1.

pyridinium model as basis underestimate it. A compromise between these two models is required. We therefore compute the line positions directly by taking an appropriate linear combination of the values (τ_A) for an aromatic pyridine and (τ_B) for an aromatic pyridinium model and adjusting a full ring-current contribution of $r = 0{\cdot}4$ p.p.m. for the assumed fractional aromaticity, x. Calculated values are then given by the expression (i). The second term in (i) corrects for the partial development of the zwitterion and the third

$$\tau_{calc.} = \tau_A - x(\tau_A - \tau_B) + (1 - x)r \quad . \quad . \quad . \quad . \quad \text{(i)}$$

term for the partial loss of ring current. By trial and error it appears that a value of $x = 0{\cdot}31$ gives the best fit between calculated line positions for methyl-protons ($\tau_{calc.}$) and those experimentally observed ($\tau_{obs.}$) for 2-pyridones, the results being shown in Table 4.

TABLE 4. *Proton resonance values* ($\tau_{obs.}$)[a] *for* C-*methyl substituents of* 1-*methyl*-2-*pyridones compared with values* ($\tau_{calc.}$) *calculated from eqn.* (i) *with* $x = 0{\cdot}31$.

Me position	τ_A	τ_B	$\tau_{calc.}$	$\tau_{calc.} - \tau_{obs.}$
3	7·74	7·40	7·91	0·06
4	7·72[b]	7·44[d]	7·91	0·02
5	7·74	7·40	7·91	−0·01
6	7·43[c]	7·04[e]	7·59	−0·06

(*a*) As in Table 2. (*b*) Average of values for compounds (8) and (12), (*c*) of those for (8), (9), (11), and (12), (*d*) of those for (14), (15), and (17), and (*e*) of those for (13), (14), (15), and (17) of Table 1.

It is encouraging that this approach and the first give reasonably consistent results, *viz.*, 31% and 36% of aromatic character. Again the agreement between calculated and observed values is poor for the 6-position. The equally poor agreement between the values for the 3-position (Table 4) results from three shielding effects operative at the methyl-protons there which have not been considered. These are a diamagnetic shift resulting from induction by the partial negative charge on the oxygen atom, a paramagnetic shift caused by hydrogen bonding between the 3-methyl group and the negatively

[13] See, *e.g.*, Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, p. 106.

charged oxygen, and a paramagnetic shift associated with the diamagnetic anisotropy of the partial carbonyl double bond. It is not feasible to allow precisely for these three effects but it is unlikely that the net correction would exceed 0·1 p.p.m.

We have also attempted an " analysis " of the shifts of the ring protons, using equation (i). We have used the proton line positions for pyridine for τ_A and have derived values for $(\tau_A - \tau_B)$ from the data for the ring protons in the lutidines (8), (9), and (10) and their quaternary salts listed in Table 1. The value r for the contribution of the ring current to the shielding of the protons in benzene has been taken as 1·55 p.p.m., being the difference between the τ value for benzene (2·73) and the average of the τ values for cyclo-octatetraene (4·31) and cyclo-octatriene (4·26).[14] We have also included a correction of $0{\cdot}4x$ p.p.m. to the shift of the 3-proton to allow for the partial negative pole on oxygen, attached at the 2-position.* We find the best fit between calculated and observed proton resonance values is obtained with $x = 0{\cdot}38$ (Table 5). However, the agreement between individual results is much worse than for the methyl-protons. This means that the charge density at the various carbon atoms in the 2-pyridones is certainly very different from that in the corresponding pyridines; for instance it appears that the 4-position has a lower charge density in a pyridone ring than in the pyridine.

The three completed analyses (Tables 2, 4, and 5) are in fair agreement and suggest that the 2-pyridone ring system has $35 \pm 5\%$ of the aromatic character of benzene as defined by ability to sustain a ring current.

TABLE 5. *Calculated (on the basis $x = 0{\cdot}38$) and observed ring proton τ values for 1-methyl-2-pyridone.*

H position	τ_A [a]	$(\tau_A - \tau_B)$ [b]	$\tau_{calc.}$ [c]	$\tau_{obs.}$ [d]	$\tau_{calc.} - \tau_{obs.}$
3	3·01	1·02	3·73	3·43	0·30
4	2·64	0·91	3·25	2·74	0·51
5	3·01	1·00	3·59	3·85	−0·26
6	1·50	0·98	2·09	2·69	−0·60

[a] Values for compound (7) of Table 1. [b] Average differences between ring proton τ values in (8), (9), and (10) and their quaternary salts, from Table 1. [c] See text. [d] Values for (1) in Table 1.

The percentage of aromatic character could in principle be calculated from dipole-moment data but there is the difficulty of assigning a moment to model (A). Nevertheless it is reasonable to suppose that the observed figure of 4·12 D could be accounted for by ~35% of aromatic character in 1-methyl-2-pyridone.

In terms of resonance energy, this degree of aromaticity would correspond to a stabilisation of 12~15 kcal. mole^{-1} † which is reflected in the chemical properties of the 2-pyridones. These compounds show well-marked aromatic properties and do not behave as unsaturated lactams, in spite of there being much evidence to indicate that they exist essentially in the 2-pyridone form (I*a*) and not as 2-hydroxypyridines (I*b*).[15] Thus there are no reports of the addition of maleic anhydride across the 3,6-positions, *i.e.*, across the formal diene system of structure (I*a*). Indeed we have tried the Diels–Alder

reaction of maleic anhydride with 1-methyl-2-pyridone and its 4,6-dimethyl homologue, and find no evidence of addition under conditions where the corresponding 2-pyrones react

* The effect (0·4) of the$^+$ negative pole in H–C–C–O$^-$ is taken as 0·33 of the difference in τ value between $H_3C{-}N<$ and $H_3C{-}N<$.

† This value is based on the resonance energy of benzene and on the assumption that there is approximate correspondence between resonance energy and chemical-shift data as measures of aromatic character.

[14] Tiers, personal communication.
[15] Ref. 6, pp. 55—62.

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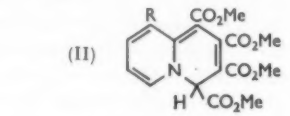
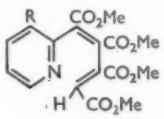
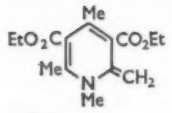
readily. Further, 2-pyridones are not cleaved by alkali, and they and their *N*-alkyl derivatives readily undergo electrophilic substitution in the 3- and the 5-position with a variety of reagents.[16] Whilst the chemical results suggest that 2-pyridones are aromatic, there has hitherto been no simple means of assessing their aromaticity.

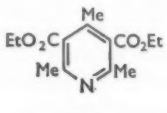




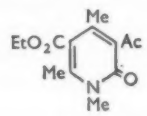
(III)



(18)



(12)



(6)

Recently,[17] it was suggested that nuclear magnetic resonance spectroscopy could not distinguish between the formulations (II) and (III) for adducts of pyridine (R = H) and of 3-picoline (R = Me) with acetylenedicarboxylic ester, because at the time there was no information regarding the magnitude of a possible ring current in (II). Our present results make it clear that the structure (II) could not give rise to a ring current of a sufficient magnitude to account for the observed positions of the ring and methyl-protons. Indeed we have confirmed this by comparing the spectrum of the 1,2-dihydro-2-methylenepyridine (18), which is a very labile compound, with that of the analogous methylpyridine (12). The τ values for the ring methyl groups in the compound (18) correspond to the virtual absence of a ring current. Presumably systems such as (18) are less aromatic than a corresponding pyridone (6), and perhaps not at all aromatic, because of the lower tendency of carbon than of oxygen to accept a negative charge. To accommodate the chemistry, it is possible to formulate each of the preceding adducts as a mixture of ring-chain tautomers,[18] (II) and (III), in which case the equilibrium must be very rapidly established and must be well towards (III).

Interpretations of Spectra.—The spectrum of 1-methyl-2-pyridone (1) contains a complex band around τ 2·7, a triplet at 3·85, and a doublet at 3·43. The coupling between the 3- and the 5-proton is very small (~1 c.) so that the centres of gravity of the two high-field multiplets will be a good approximation to the chemical shifts. The line positions of the 4- and the 6-proton were then found by using a proton–proton double irradiation technique (developed in these Laboratories by Dr. D. W. Turner) details of which are being described elsewhere.

The 1,3-dimethyl-2-pyridone (2) approximates to an A_2X nuclear-spin system. The 1,5-dimethyl-2-pyridone (3) gives rise to an ABC system, but the chemical shift between the strongly coupled 3- and 4-protons is sufficiently large to allow a first-order analysis. The spectrum of the 1,6-dimethyl-2-pyridone (4) can similarly be analysed because the 4-proton, which is involved in strong coupling with the 3- and the 5-proton, has a line position well removed from the others. The lines in the spectrum of 1,4,6-trimethyl-2-pyridone (5) are assigned on the basis of the chemical-shift data for the preceding pyridones. The assignments for the pyridone (6) follow similarly, the only difficulty then being distinction between the methyl group at the 6-position and that of the 3-acetyl substituent. However, the band at 7·48 is much the sharpest line in the spectrum and therefore is best regarded as arising from the protons of the 3-acetyl group.

The ring protons of the 2,6- and 3,5-lutidines, (9) and (10), and their quaternary salts,

[16] Rodd, "Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1957, Vol. IVA, pp. 544—546; Elderfield, "Heterocyclic Compounds," Wiley, New York, 1950, Vol. I, pp. 534—537.
[17] Jackman, Johnson, and Tebby, *J.*, 1960, 1579; cf. Acheson and Taylor, *ibid.*, p. 1691.
[18] Cf. van Tamelen, Aldrich, Bender, and Miller, *Proc. Chem. Soc.*, 1959, 309.

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(13) and (16), are by symmetry A_2B nuclear-spin systems, and those of 2,4-lutidine (8) and its quaternary salt (14) approximate to the same type.

In the spectrum of the 1,2-dihydro-2-methylenepyridine (18) we have assigned the more deshielded of the two *C*-methyl absorptions to that of the 6-methyl substituent because in the other compounds proximity to the ring-nitrogen results in a paramagnetic shift. The low-field methyl is assigned to that attached to nitrogen. The compound was obtained in the previously described orange and yellow forms [19] but it did not prove possible to obtain distinct spectra corresponding to these supposed 4- and 2-methylene tautomeric forms, even by employing deuterochloroform and Bu^{t}OD, respectively, and examining the solutions as rapidly as possible. In addition to the strong bands listed in Table 1, there were weak bands at 8·02 and 6·87 which could be attributed to methyl and methylene in the 4-methylene system. The spectrum therefore is consistent with the existence of compound (18) as a tautomeric mixture in which the 2-methylene form predominates.

Experimental

The nuclear magnetic resonance spectra were determined with a Varian 4300 spectrometer with a 56·4 Mc. oscillator. The measurements were made at 21° on 5% solutions in deuterochloroform containing 0·5% of tetramethylsilane as internal reference. The spectra were calibrated by the side-band technique with the aid of a Muirhead-Wigan D-695-A decade

Compound No.[a]	Ref.[b]	M. p., or b. p.; n_D[c]	Found (%) C	H	N	Formula	Calc. (%) C	H	N
1	20	82°/0·3 mm. n_D^{20} 1·5684	65·9	6·3	12·7	C_6H_7NO	66·0	6·5	12·8
4	21	57—58°	68·2	7·4	11·5	C_7H_9NO	68·3	7·4	11·4
5	19	89° [e]	69·9	7·9	10·4	$C_8H_{11}NO$	70·0	8·1	10·2
6	19	91—92°	62·1	6·8	5·65	$C_{13}H_{17}NO_4$	62·1	6·8	5·6
8	Com.	157° n_D^{22} 1·4997	78·05	8·4		C_7H_9N	78·45	8·5	
9	,,	143° n_D^{21} 1·4983	78·3	8·4		,,	,,	,,	
10	,,	170° n_D^{24} 1·5031	78·6	8·6		,,	,,	,,	
11	[d]	73°	61·9	6·7	5·9	$C_{13}H_{17}NO_4$	62·1	6·8	5·6
12	[e]	185°/15 mm. n_D^{22} 1·4938	63·4	7·2	5·3	$C_{14}H_{19}NO_4$	63·4	7·2	5·3
15	22	178° [f]	38·3	4·6		$C_8H_{13}IN$	38·6	4·85	
16	23	270°	38·8	4·65	5·2	,,	,,	,,	5·6
17 (metho-sulphate)	19	182° [g]	49·2	6·4	3·6	$C_{16}H_{25}NO_8S$	49·1	6·4	3·6
18	19	Orange, 69°	64·4	7·5		$C_{15}H_{21}NO_4$	64·5	7·6	
		Yellow, 74°	64·6	7·6	5·3	,,	,,	,,	5·0
19	24	75°/16 mm. n_D^{21} 1·5020	66·4	7·75		$C_7H_{10}O_2$	66·6	8·0	

[a] As in Table 1. [b] Reference to method of preparation; "Com." signifies commercial origin. [c] Lit., m. p. 84—85°. [d] From the 1,4-dihydro-compound [25] by warming with 2N-nitric acid (7 parts) and concentrated nitric acid (1 part) for 15 min. and then adding an excess of ammonia. [e] By similar oxidation of the 1,4-dihydro-compound.[26] [f] Lit., m. p. 118°. [g] Lit., m. p. 172—174°.

oscillator, each of the results which appear in Table 1 being the average of at least four separate determinations. All compounds (see Table) were purified and the spectra were consistent with the compounds' being pure.

[19] Mumm and Hingst, *Ber.*, 1923, **56**, 2301.
[20] Prill and McElvain, *Org. Synth.*, Coll. Vol. II, p. 419.
[21] Adams and Schrecker, *J. Amer. Chem. Soc.*, 1949, **71**, 1186.
[22] Takahashi and Satake, *J. Pharm. Soc. Japan*, 1954, **74**, 135.
[23] Oparina, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2001.
[24] Posner and Rohde, *Ber.*, 1910, **43**, 2665; Farmer and Morrison-Jones, *J.*, 1940, 1339.
[25] Singer and McElvain, *Org. Synth.*, Coll. Vol. II, 214.
[26] Haley and Maitland, *J.*, 1951, 3155.

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1,3-*Dimethyl-2-pyridone* (2).—By Adams and Schrecker's methods,[21] 1-amino-3-picoline (7·3 g.) was converted into 3-methyl-2-pyridone (4·5 g.), m. p. 137—139°, and methylated to 1,3-*dimethyl-2-pyridone* (4·5 g.) which after fractionation had b. p. 78°/0·5 mm., n_D^{24} 1·5550 (Found: C, 68·3; H, 7·2. C_7H_9NO requires C, 68·3; H, 7·4; N, 11·4%), $\nu_{max.}$ (film) 2911m (C–H), 1649s (C=O), 1595s and 1559m (double bonds) cm.$^{-1}$.

1,5-*Dimethyl-2-pyridone* (3).—Similarly, 1-amino-5-picoline (9·3 g.) was transformed into 1,5-dimethyl-2-pyridone (6·3 g.), b. p. 98°/3·5 mm., which after further fractionation had m. p. 40—41° and was very hygroscopic (Found: C, 67·9; H, 7·4; N, 11·1%); it had $\nu_{max.}$ (in CCl_4) 2911m (C–H), 1699s (C=O), 1605s and 1528w (double bonds) cm.$^{-1}$.

2,6-*Lutidine Ethiodide* (13).—The components were refluxed together for 10 hr., and the *salt* was crystallised from acetone to give prisms, m. p. 240—242° (Found: C, 41·35; H, 5·55; N, 5·0. $C_9H_{14}IN$ requires C, 41·1; H, 5·4; N, 5·3%).

2,4-*Lutidine Ethiodide* (14).—Prepared by refluxing the components together for 2·5 hr., the *salt* crystallised from t-butyl alcohol as felted needles, m. p. 106° (Found: C, 41·1; H, 5·25%).

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182. *Conjugated Macrocycles. Part XXXII.* Absorption Spectra of Tetrazaporphins and Phthalocyanines. Formation of Pyridine Salts.*

By MARGARET WHALLEY.

Metal-free tetrazaporphins in pyridine solution give absorption spectra similar to those of their metal derivatives. This is apparently because pyridinium salts are formed. The electronic absorption spectra of a number of metal phthalocyanines have been redetermined. The composition of the unusual stannic phthalocyanine has been confirmed.

THE absorption spectra of metal-free tetrazaporphins in, *e.g.*, chlorobenzene or 1-chloronaphthalene normally show two bands of high intensity in the visible region.[1] However, solutions of these compounds in pyridine (free from metal ions) can show spectra similar to those of the metal tetrazaporphins, *i.e.*, with a single intense band in the visible region. The metal derivatives of tribenzotetrazaporphin show two intense peaks in the visible

TABLE 1. *Light absorptions of tetrazaporphin pyridinium salts in pyridine.*

Pyridinium salt from	Method	$\lambda_{max.}$ (mμ)
Tetrazaporphin	*a*	576, 530, 332 ($E^{1\%}_{1\,cm.}$ 547, 93, 336)
Tetramethyltetrazaporphin	*a*	581, 546
Octamethyltetrazaporphin	*a*	595, 547
Tetracyclohexenotetrazaporphin	*a*	595, 548
Tribenzotetrazaporphin	*b*	663, 626, 590
Phthalocyanine	*c*	672, 644

Methods: *a*, Anærobic irradiation of a pyridine solution with collimated light from a " Pointolite " lamp at 25 cm. *b*, Keeping a pyridine solution in the absence of air for 7 days. *c*, Extraction into pyridine in a Soxhlet apparatus.

region,[2] but again there is a close similarity between their spectra and that of the metal-free pigment in pyridine. The conditions under which these pyridine solutions with anomalous absorption spectra are formed, together with their absorption maxima in the visible region, are given in Table 1. The tetrazaporphin product was the only one isolated. It seems

* Part XXXI, *J.*, 1958, 3879.

[1] Linstead and Whalley, *J.*, 1952, 4839; Ficken and Linstead, *J.*, 1952, 4846; Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521; Brown, Spiers, and Whalley, *J.*, 1957, 2882; Elvidge and Linstead, *J.*, 1955, 3536.

[2] Elvidge, Golden, and Linstead, *J.*, 1957, 2466.

likely that the tetrazaporphins form pyridinium salts because the two central hydrogen atoms of the macrocycles are known to be weakly acidic. These salts, which would be expected to show spectra of the metal tetrazaporphin type, would readily dissociate into their components. Dissociation indeed occurs on dissolution in solvents such as chlorobenzene, except for the tetrazaporphin product which is surprisingly stable.

Good evidence for the pyridinium salt structure comes from the infrared absorption characteristics of the tetrazaporphin–pyridine compound, given in Table 2. Also listed

TABLE 2. *Infrared absorptions in* KBr *disc* (*principal max. in cm*$^{-1}$)

Tetrazaporphin pyridinium salt	Tetrazaporphin	Magnesium tetrazaporphin	Assignment
	3236w		N–H stretch
3067w, 2915s, 2841s	3044	3067, 2915, 2849m	C–H
2012, 1953d			$^{+}$N–H [3]
1755—1575b		1755—1560b	
1709			C=NH^{+} [4]
1529w, 1464	1550, 1504, 1477	1572w, 1512s, 1463	C=C, C=N
1403w, 1377w, 1260, 987, 800	1424w, 1339w, 1244w, 1225w, 1182w, 1033s, 939s, 825s, 789s, 718s	1412, 1406w, 1316 1240s, 1045s, 968s, 793s, 746s	Skeletal vibrations

s = strong, w = weak, d = doublet, b = broad (medium intensity unspecified).

for comparison are the data for tetrazaporphin and magnesium tetrazaporphin. The spectrum of the pyridinium salt shows a doublet at 2012, 1953 cm.$^{-1}$ ascribed [3] to pyridinium $^{+}$N–H and a peak at 1709 cm.$^{-1}$ which may be due to C=NH^{+}.[4] Further, it shows a broad region of absorption at 1755—1575 cm.$^{-1}$, as in the spectrum of magnesium tetrazaporphin.

Previous determinations of the electronic absorption spectra of phthalocyanines involved visual instruments [5] or unusual solvents.[6] The results of recent redeterminations made with photoelectric instruments on carefully purified samples are now recorded. These data, assembled in Table 3, are considered to be accurate and replace those previously published. Quantitative spectral details for palladium and cobalt phthalocyanine are given for the first time. The spectrum of metal-free phthalocyanine and those of its metal derivatives, here examined, all showed the single band at *ca.* 350 mμ which is characteristic of tetrazaporphins. The visible spectra of the phthalocyanine complexes of bivalent Cu, Ni, Co, Fe, Zn, Pd, and Mg were very similar to one another, having a single, narrow, intense band in the 650—675 mμ region. The spectrum of magnesium phthalocyanine is thus different from that reported earlier by Barrett *et al.*[5] The positions of the additional peaks then found correspond to those of metal-free phthalocyanine which may have been formed by traces of hydrochloric acid in the solvent (1-chloronaphthalene). I find that magnesium phthalocyanine which has been crystallised from pyridine, contrary to a previous report,[7] is not contaminated with metal-free pigment.

Stannic phthalocyanine is unusual in containing two phthalocyanine residues for each atom of tin.[8] It would be expected that the spectrum of such a compound would differ from those of the typical metal phthalocyanines but this had not been measured. Stannic phthalocyanine was obtained as before [8] by reaction of dichlorostannic phthalocyanine with disodium phthalocyanine, and the partially purified product was then chromatographed on alumina to remove small amounts of metal-free and dichlorostannic phthalocyanine. The chromatography established that the stannic phthalocyanine was

[3] Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166.
[4] Cf. Leonard and Gash, *J. Amer. Chem. Soc.*, 1954, **76**, 2781.
[5] Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151; Barrett, Linstead, Rundall, and Tuey, *J.*, 1940, 1079.
[6] Evstigneev and Krasnovskii, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 1399.
[7] Evstigneev and Krasnovskii, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 417.
[8] Barrett, Dent, and Linstead, *J.*, 1936, 1719.

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homogeneous and not a mixture or molecular complex of stannous phthalocyanine and phthalocyanine. Elementary analysis and quantitative oxidation [9] of the crystallised pigment agreed with the constitution reported previously.[8] The light absorption is, indeed, unusual: the spectrum shows a strong band at 626 mμ and a weaker one at the very end of the visible region, at 774 mμ. The nature of the bonding in this unique compound, about which speculation can be made, should become clear from the results of an *X*-ray or electron-diffraction crystallographic examination

TABLE 3. *Visible and ultraviolet absorptions.*

Phthalocyanines		$\lambda_{max.}$ (Å) (and $\log_{10}\varepsilon$)									
Metal-free	*a*	3500				5540		6020	6380	6650	6980
		4·74				3·57		4·43	4·62	5·18	5·21
* Cu	*a*	3500		5100	5260	5670	5880	6110	6480	6780	
		4·76		3·56	3·57	3·91	4·06	4·56	4·51	5·34	
Ni	*a*	3510				5600	5800	6030	6430	6710	
		4·57				3·75	3·82	4·51	4·47	5·10	
Co	*a*	3480						6065		6720	
		4·65						4·53		5·19	
* Co	*b*	3300						5965		6575	
		4·86						4·51		5·07	
Fe·2py	*b*	3295	4140					5930		6540	
		4·88	4·29					4·47		5·03	
Fe	*c*	3300						5950		6560	
		4·68						3·95		4·84	
Zn·py	*b*	3475						6070	6460	6720	
		4·81						4·59	4·56	5·45	
* Mg·H_2O	*b*	3470				5680	5870	6100	6470	6745	
		4·73				3·59	3·79	4·45	4·39	4·94	
* Pd	*a*	3470				5570	5765	5955	6330	6605	
		4·69				3·98	4·07	4·57	4·51	5·32	
Sn diphthalocyanine	*d*	3380						5755		6260	7740
		5·11						4·33		5·06	4·57
Tetrazaporphin											
* Co tetracyclohexeno	*c*	3515						5395		5890	
		4·72						4·17		4·95	

a, 1-Chloronaphthalene; *b*, pyridine; *c*, *o*-dichlorobenzene; *d*, chlorobenzene.
* With Dr. G. E. Ficken.

Lead phthalocyanine is too readily demetallated in dilute solution for accurate spectral details to be obtained. Thus in 1-chloronaphthalene the spectrum is that of metal-free phthalocyanine, and, in pyridine, bands corresponding to phthalocyanine and the pyridinium salt were obtained.

An improved method for the preparation of cobalt tetracyclohexenotetrazaporphin (cf. Ficken *et al.*[1]) is described, and spectral details are included in Table 3.

EXPERIMENTAL

Tetrazaporphin–Pyridine Salt.—A freshly boiled solution of tetrazaporphin (30 mg.) in pyridine (500 c.c.) containing a trace of quinol or pyrogallol was irradiated (in portions) in completely filled 2-cm. cells in the light-path of a Hilger–Nutting visual spectrophotometer: the change was followed spectroscopically and required 1—10 hr./cell-full. The combined products were evaporated to dryness and the blue solid was washed several times with methanol and then crystallised extractively from chlorobenzene to give the pyridine salt (2·6 mg.) (for the infrared spectrum see Table 2).

Purification of Phthalocyanines.—The pigments (see Table) were prepared by methods previously described [1,8,10] and were purified by extractive crystallisation from 1-chloronaphthalene (A), *o*-dichlorobenzene (B), or pyridine (C), with the exception of ferrous phthalocyanine which was obtained pure by sublimation at 350°/10^{-6} mm. of the dipyridine solvate.

[9] Elvidge, following paper.
[10] Barrett, Frye, and Linstead, *J.*, 1938, 1157.

Phthalocyanine		Found C	Found H	Found N	Found Metal	Calc. C	Calc. H	Calc. N	Calc. Metal
Metal-free	(A)	74·3	3·9	21·6	—	74·7	3·5	21·8	—
Cu	(A)	66·7	3·1	19·25	11·3	66·7	2·8	19·5	11·0
Ni	(A)	67·1	3·1	19·5	10·2	67·3	2·8	19·6	10·3
Co	(B)	67·4	3·1	19·8	10·1	67·3	2·8	19·6	10·3
Fe,2py *	(C)	69·3	3·8	18·9	7·7	69·4	3·6	19·3	7·7
Fe		68·0	2·9	19·7	9·95	67·6	2·8	19·7	9·8
Zn,py	(C)	67·7	3·5	19·3		67·6	3·2	19·2	
Mg,H_2O	(C)	69·6	3·7	19·5	4·5	69·3	3·3	20·2	4·4
Pd	(B)	61·7	2·8		17·0	62·1	2·6		17·2
Pb	(C)	53·9	2·25	15·6	27·9	53·4	2·2	15·6	28·8

* py = pyridine.

Solutions for spectroscopic examination were prepared by boiling the pigment (0·4—0·6 mg.) with solvent for 5—10 min., cooling the solution, and making the volume up to 100 c.c. Determinations, made with Unicam S.P. 500 and S.P. 600 spectrophotometers, were then completed within 1 hr.

Stannic Phthalocyanine (cf. ref. 8).—Dichlorotin(IV) phthalocyanine (250 mg.) and disodium phthalocyanine (200 mg.) were refluxed in 1-chloronaphthalene (50 c.c.) for 1·5 hr. and the hot solution was filtered from sodium chloride. When the solution had cooled, the metal-free phthalocyanine (140 mg.) which had separated was filtered off. Concentration of the filtrate under reduced pressure afforded a solid, mainly stannic phthalocyanine, which was extracted into benzene (*ca.* 500 c.c.), and the solution was chromatographed on alumina (Spence, type H; 8 × 4·5 cm.). Traces of metal-free phthalocyanine were strongly adsorbed at the top of the column. Dichlorotin phthalocyanine formed a slow-moving green band, and stannic phthalocyanine a blue band which was rapidly eluted with benzene–methanol (20 : 1). The blue solid from evaporation of the eluate was crystallised extractively four times from benzene, the hot solution being filtered each time under gravity through Whatman no. 50 paper to remove traces of alumina. Stannic phthalocyanine was obtained as minute dark blue prisms (Found: C, 67·4; H, 3·1; N, 19·6; Sn, 9·9. Calc. for $C_{64}H_{32}N_{16}Sn$: C, 67·2; H, 2·8; N, 19·6; Sn, 10·4%).

Cobalt Tetracyclohexenotetrazaporphin (with Dr. G. E. Ficken).—Magnesium tetracyclohexenotetrazaporphin monohydrate monopyridine solvate (Ficken *et al.*[1]) (152 mg.) was extracted into a solution of anhydrous cobalt acetate (157 mg.) in dry 2-ethoxyethanol. The solid which separated from the cooled solution was filtered off, washed with hot dilute hydrochloric acid, water, and ethanol, and dried. Extractive crystallisation from *o*-dichlorobenzene gave cobalt tetracyclohexenotetrazaporphin (133 mg., 93%) (Found: C, 65·45; H, 5·7; N, 19·3; Co, 9·9. Calc. for $C_{32}H_{32}CoN_8$: C, 65·4; H, 5·5; N, 19·1; Co, 10·0%).

I thank Sir Patrick Linstead, C.B.E., F.R.S., for his interest.

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183. *Metal Chelates. Part I. A Micromethod for the Determination of the Valency of a Metal in a Phthalocyanine Complex.*

By J. A. Elvidge.

0·01N-Dichromate disrupts the large ring of many metal phthalocyanines and substituted tetrazaporphins without causing dehydrogenation. Titration with this reagent thus permits the valency state of the metal to be determined.

During attempts to determine the hydrogenation level of hydrotetrazaporphins,[1] it was found that 0·01N-dichromate effects oxidative hydrolysis of the macrocyclic ring, quantitatively, without effecting dehydrogenation, in contrast to the behaviour of other

[1] Ficken, Linstead, Stephen, and Whalley, *J.*, 1958, 3879.

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oxidants.[2,3] It then appeared that if the reagent proved equally specific with tetrazaporphin metal derivatives, a ready method would be available for confirming the valency of the metal. Good results are obtained with metal phthalocyanines (see Table); metal tetrazaporphins give results consistently slightly high, but nevertheless useful.

The disruption of a phthalocyanine or tetrazaporphin ring requires 1 atom-equivalent of oxygen and gives 4 mols. of imide.[2] There is little interference under our conditions from substituents (in the cases examined). The observed oxygen uptake by a metal derivative will differ from 1 atom-equivalent only if the metal ion which is liberated subsequently undergoes valency change with the reagents. This will be known. Consequently the valency state of the metal in a tetrazaporphin complex can be deduced from the observed oxygen uptake.

The method gives results with substituted tetrazaporphins in agreement with previously assigned constitutions. The only exception is the parent tetrazaporphin and its metal complexes. These consume considerably more than 1 atom-equivalent of oxygen, evidently because the first-formed maleimide is unstable even to very dilute dichromate.[4] The method confirmed that the iron in iron phthalocyanine [5] and also in the octahedral dipyridine–iron complex [6] is in the bivalent state, but is tervalent in chloroiron phthalocyanine.[6] Zinc phthalocyanine [5] and its monopyridine solvate [7] gave results similar to one another and to that from zinc chlorophthalocyanine,[5] so that in the latter the metal is bivalent and the chlorine a peripheral substituent. The aluminium in chloroaluminium phthalocyanine [5] is tervalent as expected, the chlorine being an anionic ligand, as must be the chlorine atoms in dichlorotin phthalocyanine [5] which gave a result indicative of quadrivalent tin. Tin phthalocyanine [5] and tin diphthalocyanine [5] did not give quite such accurate results, but these nevertheless clearly indicate respectively bivalency and quadrivalency for the metal. The phthalocyanine complexes of bivalent cobalt,[5] copper,[8] lead,[5] and nickel [5] afforded expected results, although the last complex was perceptibly less easily oxidised and this necessitated a slight modification of the procedure. The only complex examined that failed to undergo oxidation smoothly by our procedure was platinum phthalocyanine. Its extreme resistance to oxidation has previously been mentioned.[9]

Most recently, the method has been used to confirm the valency states of the metal in the newly isolated phthalocyanine chromium(II) and chromium(III) hydroxide complexes.[10] Further uses are likely to arise.

Experimental

Quantitative Oxidation.—The samples used were analytically pure. The tetrazaporphin pigment (4—6 mg.; powdered in an agate mortar) was weighed accurately into a 50 c.c. conical flask. A lead, from a supply of dry nitrogen, was hung over the side of the flask. As soon as the air had been displaced, concentrated sulphuric acid (3·0 c.c.) was pipetted in, and the pigment dissolved (by swirling). The flask was placed in crushed ice, and ice (from 3·0 c.c. of boiled-out distilled water) was added, followed *immediately* by 5·0 c.c. of 0·01N-potassium dichromate from a pipette, whilst the flask was gently swirled. By the time the pipette was empty, the pigment had been destroyed and the (hot) solution had regained room temperature. 0·01N-Ferrous sulphate (5·0 c.c.) was added, followed by internal indicator, *viz.*, 1·5 c.c. of acid (an aqueous solution containing 15 c.c. of sulphuric acid and 15 c.c. of syrupy phosphoric acid

[2] Dent, Linstead, and Lowe, *J.*, 1934, 1033.
[3] Ficken and Linstead, *J.*, 1952, 4846; Linstead and Weiss, *J.*, 1950, 2981.
[4] Cf. Linstead and Whalley, *J.*, 1952, 4839.
[5] Barrett, Dent, and Linstead, *J.*, 1936, 1719.
[6] Barrett, Frye, and Linstead, *J.*, 1938, 1157.
[7] Whalley, preceding paper.
[8] Dent and Linstead, *J.*, 1934, 1027.
[9] Ref. 5, p. 1734.
[10] Elvidge and Lever, *J.*, 1961, in the press.

in 100 c.c.) and 2 drops of 0·2% barium diphenylaminesulphonate, and the solution was titrated with the dichromate until a violet colour appeared.

Nickel phthalocyanine was oxidised smoothly if the sulphuric acid solution of the pigment was not cooled before addition of ice and oxidant.

The results are tabulated.

Pigment	*M*	Weight (mg.)	Titre (c.c.; 0·01N)	Atoms of O consumed: Obs.	Calc.	Valency of metal
Tetrazaporphins (ref. 1, except as indicated)						
Me_8	426	4·35	1·86	0·91	1·0	
		3·60	1·63	0·97		
H_4Me_8	430	4·70	1·13	1·03	,,	
		4·80	1·18	1·06		
Co Me_8 (ref. 11)	483	3·86	2·07	1·30	,,	2
		3·34	1·79	1·30		
Ni Me_8 (ref. 11)	483	3·16	1·64	1·25	,,	,,
Ni Me_4 (ref. 12)	427	4·67	2·70	1·24	,,	,,
Tetracyclohexeno	530	4·12	1·54	0·99	,,	
H_4 tetracyclohexeno	534	4·23	1·61	1·01	,,	
Phthalocyanines (ref. 7, except as indicated)						
Fe	568	4·02	1·99	1·41	1·5	2
		4·29	2·23	1·47		
		4·62	2·38	1·46		
Fe, 2py	726	4·47	1·77	1·44	,,	,,
		4·65	1·97	1·54		
FeCl (ref. 6)	603·5	4·03	1·28	0·96	1·0	3
		4·68	1·54	0·99		
Zn (ref. 5)	577·5	4·27	1·53	1·03	,,	2
Zn.py	656·5	4·23	1·40	1·08	,,	,,
Zn chlorophthalocyanine (ref. 5)	612	5·29	1·74	1·01	,,	,,
		5·42	1·62	0·91		
AlCl (ref. 5)	574·5	5·41	2·10	1·11	,,	3
		5·29	1·94	1·05		
		5·36	1·96	1·05		
$SnCl_2$ (ref. 5)	702	5·81	1·82	1·10	,,	4
		4·81	1·62	1·18		
		5·30	1·76	1·16		
Sn (ref. 5)	603	5·19	2·87	1·74	2·0	2
		5·64	3·31	1·85		
Sn diphthalocyanine	1143	5·22	1·73	1·89	,,	4
		4·82	1·60	1·90		
Co	571	5·19	2·19	1·15	1·0	2
		5·18	1·93	1·06		
Cu	575	4·62	1·80	1·12	,,	,,
		4·18	1·58	1·08		
Ph	719	4·34	1·20	0·99	,,	,,
		5·17	1·34	0·91		
Ni	571	4·96	1·87	1·07	,,	,,

I am grateful to Sir Patrick Linstead, C.B.E., F.R.S., for some phthalocyanine specimens.

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[*Received, July 27th,* 1960.]

[11] Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521
[12] Brown, Spiers, and Whalley, *J.*, 1957, 2882.

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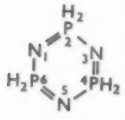
184. *Phosphorus–Nitrogen Compounds. Part I. Alkylamino- and Dialkylamino-derivatives of Cyclotriphosphazatriene.*

By S. K. Ray and R. A. Shaw.

Reaction of hexachlorocyclotriphosphazatriene with primary (Me—Bu^n) alkylamines results in complete aminolysis at or near room temperature. In similar circumstances branched alkylamines (Pr^i, Bu^i, Bu^s, Bu^t, cyclohexyl) yield partially substituted derivatives and higher temperatures are required for complete substitution. These effects are more pronounced with secondary amines (R in NHR_2 = Me, Et, Pr^n, Bu^n, Bu^i, Bu^s, cyclohexyl; piperidyl), and very bulky alkylamines failed to yield completely aminolysed compounds even under severe conditions. In reactions with dimethyl- and diethyl-amine, compounds $P_3N_3Cl_{6-n}(NR_2)_n$ were isolated with n = 1, 2, 3, 4, and 6. The stereochemistry of the ring system is discussed and structural assignments are made to some derivatives.

Nomenclature.—In this paper the hypothetical parent compound (I) is named cyclotriphospha-1,3,5-triene, with the numbering shown. Normally enumeration of the double bonds is omitted: Kekulé-type resonance is assumed. Substitution products from this parent are named by the usual methods of organic chemistry.



(I)

Although known since 1834,[1] phosphazenes have only lately been examined systematically. Until recently it was assumed [2,3] that replacement of chlorine in hexachlorocyclotriphosphazatriene occurred in geminal pairs although the only valid evidence related to two partially phenylated compounds [4] and few products had been identified where the chlorine had been partially or completely replaced.[2,5] Within the last year the isolation of products in which one [6] or three [7–10] chlorine atoms (as well as two, four, and six) had been replaced, and in particular the preparation by Becke-Goehring and John [8,9] of compounds containing both amino- and methylamino-groups, disproved the universality of pairwise replacement.

Nuclear magnetic resonance spectra of the protons in dimethylamino-derivatives,[11] and of phosphorus [9] in some other compounds, confirm the new reaction scheme proposed on chemical grounds. This proposal is that in reactions with some nitrogenous bases one chlorine on each phosphorus atom is replaced successively, and that the second chlorine atom of a pair is replaced only when no more geminal dichloro-groups are present.

Complete ammonolysis is relatively slow.[12] Although primary unbranched alkylamines (Me–Bu) react readily in ether at or near room temperature, to afford the hexasubstituted compound $P_3N_3(NHR)_6$, primary branched alkylamines (Pr^i, Bu^i, Bu^s, Bu^t, cyclohexyl) under similar conditions yield partially (usually tetra)substituted derivatives, and higher temperatures (boiling benzene, or 140—180° under pressure) are necessary for complete replacement, and from t-butylamine no product higher than the tetrasubstituted derivative could be obtained at all.

[1] Liebig, *Annalen*, 1834, **11**, 139.
[2] Cf. Audrieth, Steinman, and Toy, *Chem. Rev.*, 1943, **32**, 109.
[3] Bode, Bütow, and Lienau, *Chem. Ber.*, 1948, **81**, 547.
[4] Bode and Bach, *Ber.*, 1942, **75**, 215; Bode and Thamer, *Ber.*, 1943, **76**, 121.
[5] Cf. Steinman, Ph.D. Thesis, University of Illinois, 1942.
[6] Shaw, *Chem. and Ind.*, 1959, 412; Shaw, Conference on High Temperature Polymer and Fluid Research, Session VI, Inorganic Polymers, Dayton, Ohio, May 1959; Symposium on Macromolecules, Section IVB, Wiesbaden, October 1959.
[7] Ray and Shaw, *Chem. and Ind.*, 1959, 53.
[8] Becke-Goehring and John, *Angew. Chem.*, 1958, **70**, 657.
[9] Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.
[10] Audrieth, *Rec. Chem. Progr.*, 1959, **20**, 57; Bull, Ph.D. Thesis, University of Illinois, 1957.
[11] White, personal communication.
[12] Moureu and Rocquet, *Bull. Soc. chim. France*, 1936, **3**, 821; Audrieth and Sowerby, *Chem. and Ind.*, 1959, 748; Shaw, unpublished results.

These effects are more pronounced with secondary amines. Even dimethylamine yields, at room temperature, only a tetra-amino-compound and with most of the higher ones (Et, Pr^n, Bu^n, Bu^i, Bu^s, cyclohexyl) even the initial reaction in boiling ether is very slow. Complete substitution is achieved with dimethylamine and piperidine at 60—80°, but the others yield only partially (again usually tetra)substituted products. With diethylamine aminolysis was complete after 24 hours' heating at 150°, but with di-s-butylamine even under the most drastic conditions investigated over 95% of the starting material was recovered.

In a study with dimethyl- and diethyl-amine derivatives, $P_3N_3Cl_{6-n}(NR_2)_n$ were in each case obtained with $n = 1$, 2, 3, 4, and 6. (There were indications of isomeric compounds with NMe_2, $n = 4$, and with NEt_2, $n = 3$.)

The replacement is visualised as occurring in the stages: 2-mono, 2,4-di, 2,4,6-tri, 2,2,4,6-tetra, 2,2,4,4,6-penta, and 2,2,4,4,6,6-hexa. Proton magnetic resonance spectra of the compounds [11] in the dimethylamino-series confirm this (see Table). The mono-, di-, and tri-amino-compounds have only the amino-grouping $PCl{\cdot}NMe_2$ and give only one band. The hexa-amino-derivative, having only $P(NMe_2)_2$, gives only one, but a different band. The tetra-amino-compound, containing both groupings, shows both bands.

The reported aminocyclotriphosphazatrienes show a definite pattern. There are only two (oily) monosubstituted derivatives; this may be in part due to experimental difficulties, for there is a relatively small difference in the ease of reaction of the hexachloro- and monoamino-compounds described by us and unless great care is taken the reaction proceeds readily to the disubstituted stage. Nine disubstituted examples are available. The number of triamino-derivatives is only five, but growing, and ten tetra-amino-com-

Proton magnetic resonance spectra.

Compound	c./sec.	Compound	c./sec.
$P_3N_3Cl_5{\cdot}NMe_2$	83	$P_3N_3Cl_2(NMe_2)_4$	81 93
$P_3N_3Cl_4(NMe_2)_2$	84	$P_3N_3(NMe_2)_6$	91
$P_3N_3Cl_3(NMe_2)_3$	84		

Shifts are quoted on the high field side of water. The bands show triplet structure and the values quoted represent the mean.

pounds are known, but no penta-amino-derivatives. Twenty-four completely aminolysed compounds have been reported.

Except for a pair of tetrakisdimethylamino-derivatives and a pair of trisdiethylamino-compounds (both cases not rigidly established), no isomers have been reported in the reactions of the six-membered ring system with one reagent: it appears that one isomer is preferentially formed (or, at least, isolated). This indicates a directing effect, which could be steric and/or polar. Electronegativity considerations and the ability of phosphorus to accommodate up to twelve electrons in its valency shell point to it as the centre for nucleophilic attack. In reaction of a nucleophile Z with a cyclic structure (II), monosubstitution will yield only one product (III) (here $n = 1$, $m = 0$) (conformational isomerism being neglected). In the extreme case, where the steric requirements of X and Z are the same, disubstitution will occur at that phosphorus atom which has the lowest electron-density, *i.e.*, if Z decreases the electron-supply (relative to X) to the phosphorus atom to which it is attached [and if the assumption made below is correct that structure (VIB) is more important than (VID)], geminal disubstitution will lead to (IV); if it increases it, the second replacement will occur preferentially on another atom, leading to (V). This type of positional isomerism will be at its simplest in the six-membered ring, as the PCl_2 groups at position 4 and 6 are equivalent. In the other extreme case, with the polar effects of X and Z identical, steric requirements will predominate. With most reagents both steric and polar factors will simultaneously play a part, as well as others such as the nature of the reaction medium.

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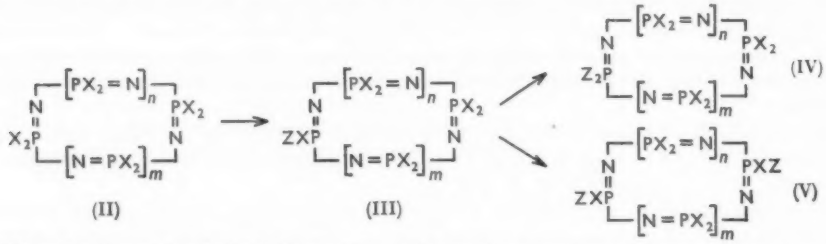
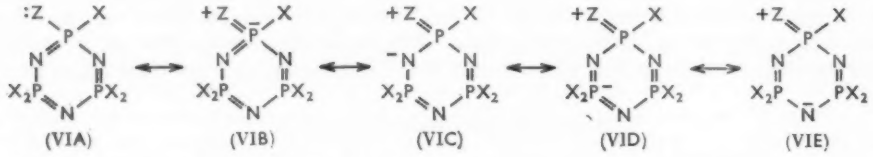
In benzenoid chemistry polar effects can be transmitted to the *meta*-position,[13] and similar effects may operate in the cyclophosphazene system where the negative charge produced by double-bond formation with the substituents could reside on the phosphorus

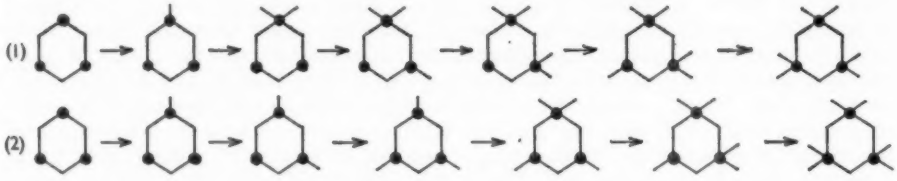


(VIB) or be transmitted (VIC, D, and E). The analogy must not be pressed too far: not only is the stereochemistry different, but whereas the benzene system contains $p\pi$–$p\pi$-bonds, the cyclophosphazenes contain $d\pi$–$p\pi$-bonds.[14] It is not known how the latter type of ring relays electronic effects, in particular whether a preferential *cis*- or *trans*-effect is exerted. Steric effects to the *meta*-position were not considered in benzene chemistry. But in the phosphazene system, where the substituents are not in the plane of the ring



(or, more generally, not in the plane of the grouping NPN), steric effects may exert some influence to the *meta*-position, in particular in the transition state, and this might be further enhanced by puckering of the ring. Non-planarity has been established for the solid state of a number of derivatives based on the eight-membered ring,[15,16] and there is *X*-ray evidence [16,17] for it in the six-membered ring system.

For successive reactions of cyclotriphosphazatrienes with one reagent, two mechanisms (1) and (2) need consideration, where ● denotes a phosphorus atom. Scheme (1) will be discussed in a later paper. The present work deals mainly with compounds derived by scheme (2).



That the amino-group produces a higher electron-density at an adjacent unsaturated centre than a chlorine atom has been shown in a number of systems; [13] and this applies more powerfully to alkylamino- and dialkylamino-groups. A phosphorus atom carrying

[13] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons Ltd., London, 1953.
[14] Craig, *Chem. and Ind.*, 1958, 3; *J.*, 1959, 997; Craig and Paddock, *Nature*, 1958, **181**, 1052.
[15] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081; Tromans, referred to by Paddock and Searle in " Advances in Inorganic Chemistry and Radiochemistry " (ed. Emeléus and Sharpe), Academic Press Inc., New York, 1959, Vol. I, p. 368; Bullen, personal communication.
[16] Jagodzinski, Langer, Oppermann, and Seel, *Z. anorg. Chem.*, 1959, **302**, 81.
[17] Pompa and Ripamonti, *Ricerca Sci.*, 1959, **29**, 1516.

an amino-group ($PNR_2{\cdot}Cl$), thus tends, by both its polar and its steric effect, to direct another molecule of a nucleophilic reagent to another PCl_2 centre, *i.e.*, in the reactions of the chlorophosphazenes with ammonia and aliphatic amines mechanism (2) would be preferred. Nuclear magnetic resonance spectra of dimethylamino-,[11] methylamino-, and amino-derivatives [9] of cyclotriphosphazatriene confirm these deductions, which must apply with greater certainty to higher amino-derivatives whose polar and steric effects would be more pronounced. The position with arylamines is less clear. Although steric factors are here less potent, polar factors are more favourable to geminal disubstitution than with ammonia. At present all results with arylamines [2,3,8] can be equally explained by either scheme. With *ortho*-diamines, especially favourable steric factors are present which may lead to the suggested spiran structure [3] [scheme (1)].

Individual differences amongst the reagents can now be considered. Correlations between the basic strengths of the amines in aqueous solution and their relative ease of reaction with the chlorophosphazenes are of little value. Brown,[18] in particular, has pointed out, that basic strength has a meaning only with reference to a given acid. Basicity in aqueous media is a measure of the polar effects. With bulkier reference acids steric effects will become increasingly important. At present no kinetic data are available for reactions of phosphazenes. In particular, as six reacting groups are available in the molecule, no strict comparison is possible after the replacement of the first chlorine atom as products $P_3N_3ZCl_5$ and $P_3N_3Z'Cl_5$ are no longer equivalent. All that can be discussed at this stage is ease of complete substitution. The results reported above show the importance of the steric factor. (Trimethylamine reacts in a superficially similar manner,[19] but a nitrogen–carbon, instead of a nitrogen–hydrogen bond is being broken.)

The small number of monoamino- and triamino-compounds isolated and the absence of a penta-amino-derivative, may be in part due to experimental difficulties. Not all the reaction mixtures were examined in the same detail as those from dimethylamine and diethylamine, and some of the compounds isolated need not represent the major products. Nevertheless the isolation of tetra-amino-derivatives, often in excellent yield, where one would have expected tri- or hexa-amino-derivatives, points to the particular stability of this structure. This is strikingly demonstrated with t-butylamine. In boiling ether a tetra-amino-compound was obtained in excellent yield, and there was no further reaction even in sealed tubes at 140—160°. Under the latter conditions, other less sterically hindered compounds, such as the tetraisopropylamino-derivative, were converted into the corresponding completely substituted hexa-amino-compound; and the tetra-t-butylamino-derivative, although resistant to further reaction with t-butylamine, reacts readily with methylamine, showing that its behaviour is largely governed by steric factors.

It has been known for some time that the phosphorus–nitrogen bonds in hexachlorocyclotriphosphazatriene are all equal, *i.e.*, resonance occurs.[20] Until recently too, all evidence pointed to the planarity of the six-membered ring.[20] However, crystallographic results [17] obtained with the chloride now indicate a planar ring slightly distorted towards a chair form. There is also possibly puckering in the corresponding fluoride.[16] If the ring is planar or near-planar the 2,2,4,6-tetra-amino-compound will probably have the 4- and the 6-group *trans* to each other. Two bulky groups would then project on either side of the ring and could present steric hindrance to a third, particularly in the transition state. (For some conformations, models show considerable interaction of bulky groups *cis* to each other.) If the ring is flexible, bulky groups may well " freeze " it into a preferred conformation (where the non-geminal groups need not be *trans* to one another), which again may hinder further reaction. Similar arguments can be invoked to a smaller extent for the prevalence of di- and the absence of penta-amino-derivatives. Thus we are dealing with a

[18] Brown, *J.*, 1955, 1248.
[19] Burg and Caron, *J. Amer. Chem. Soc.*, 1959, **81**, 836.
[20] Brockway and Bright, *J. Amer. Chem. Soc.*, 1943, **65**, 1551; Daasch, *ibid.*, 1954, **76**, 3403; Wilson and Carroll, *Chem. and Ind.*, 1958, 1558.

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structure which possesses some resemblance to benzene (unsaturation and resonance), as well as to cyclohexane (two substituents on some of the ring atoms, and the possibility of conformational isomerism). In the chemistry of carbon compounds, the directing effect of a particular group is often not exclusively to one position, and mixtures of isomers are formed; [13] the same is probably true for the phosphazenes.

Experimental

Microanalyses for carbon, hydrogen, nitrogen, and chlorine, and molecular-weight determinations were carried out by the Microanalytical Laboratory, Imperial College of Science and Technology, London.

Ether, light petroleum (unless otherwise stated of b. p. 60—80°), and benzene were dried with sodium wire. Hexachlorocyclotriphosphazatriene was prepared by Schenk and Römer's method [21] and separated by vacuum-sublimation. This product, as well as material purchased from Albright & Wilson Ltd., was recrystallised to constant m. p. from light petroleum. Silica gel (M.F.C. grade from Hopkin & Williams) was heated to the temperature and for the time stated. Amines were distilled from sodium.

2,2,4,6-*Tetrachloro*-4,6-*bismethylaminocyclotriphosphazatriene*.—Prepared by the method of Bode *et al.*[3] in 23% yield, this had m. p. 100—100·5° [from light petroleum (b. p. 40—60°)] (Found: C, 7·7; H, 2·5; Cl, 41·25; N, 21·2. Calc. for $C_2H_8Cl_4N_5P_3$: C, 7·1; H, 2·4; Cl, 42·2; N, 20·8%).

Hexamethylaminocyclotriphosphazatriene.—Excess of methylamine was added to hexachlorotriphosphazatriene (5·0 g.) in ether (150 ml.) at −78° and the mixture was then allowed to regain room temperature and filtered. The residue was extracted with cold chloroform, and light petroleum added to the extract. The resultant precipitate, recrystallised from a mixture of these two solvents, had m. p. 258° (Becke-Goehring *et al.*[9] report m. p. 258°) (2·66 g., 65%) (Found: C, 23·4; H, 8·0; N, 39·9. Calc. for $C_6H_{24}N_9P_3$: C, 22·9; H, 7·7; N, 40·0%).

Hexaethylaminocyclotriphosphazatriene.—Excess of ethylamine was added to the hexachloro-compound (5·0 g.) in benzene (50 ml.). An exothermic reaction took place. The mixture was set aside for 12 hr., filtered, and evaporated, and the residue was washed with acid, base, and water, dried, and extracted with light petroleum which, on cooling, deposited *hexaethylaminocyclotriphosphazatriene*, m. p. 118—119° (2·48 g., 43%) (Found: C, 36·5; H, 9·0; N, 32·15. $C_{12}H_{36}N_9P_3$ requires C, 36·8; H, 9·1; N, 31·6%).

Similar methods gave the *amines* recorded in the Table where variations in the solvent and conditions are stated (excess of amine was used, unless otherwise noted).

2,4-*Bismethylamino*-2,4,6,6-*tetra-t-butylaminocyclotriphosphazatriene*.—Excess of methylamine was added to 2,4-dichloro-2,4,6,6-tetra-t-butylaminocyclotriphosphazatriene (2 g.) in ether (30 ml.). The solution was kept overnight and then refluxed for 1 hr. The amine hydrochloride was filtered off, and the solvent evaporated. The residue recrystallised from light petroleum (b. p. 40—60°), yielding starting material, m. p. and mixed m. p. 156° (1·2 g., 60%). Concentrating the mother-liquor gave a solid which on recrystallisation from light petroleum yielded 2,4-*bismethylamino*-2,4,6,6-*tetra-t-butylaminocyclotriphosphazatriene*, m. p. 199° (0·31 g., 16%) (Found: C, 44·4; H, 9·0. $C_{18}H_{48}N_9P_3$ requires C, 44·7; H, 9·9%).

Pentachlorodimethylamino- and 2,2,4,6-*tetrachloro*-4,6-*bisdimethylamino-cyclotriphosphazatriene*.—Dimethylamine (2·54 g., 0·0565 mole) was added to the hexachloro-compound (10 g., 0·0288 mole) in ether (100 ml.) cooled in ice–salt. After ½ hr. the precipitate of amine hydrochloride was filtered off and the filtrate evaporated. The residue was taken up in light petroleum (b. p. 60—80°), and some hexachloro-compound (2·3 g.) was recovered by crystallisation. The mother-liquor was chromatographed on silica gel (45 g., heated at 400° for 3½ hr.) with light petroleum as eluant. The first fraction yielded hexachloro-compound (3·33 g.), the second *pentachlorodimethylaminocyclotriphosphazatriene* (2·10 g., 20%), m. p. 12—14°, b. p. 70—72°/0·01 mm. (only one peak found on gas–liquid chromatography) (Found: C, 7·1; H, 1·7; Cl, 50·8; N, 15·9. $C_3H_6Cl_5N_4P_3$ requires C, 6·7; H, 1·7; Cl, 49·7; N, 15·7%), and the third 2,2,4,6-tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene, m. p. 103° (from light petroleum) (Becke-Goehring *et al.*[9] report m. p. 103°) (1·31 g., 12%) (Found: C, 13·8; H, 3·2; Cl, 38·5; N, 19·1. Calc. for $C_4H_{12}Cl_4N_5P_3$: C, 13·2; H, 3·3; Cl, 38·9; N, 19·2%). The last

[21] Schenk and Römer, *Ber.*, 1924, **57**, 1343.

Amino-chloro-cyclotriphosphazatrienes.

No.	Amino-groups	Condns. of prep.	Yield (%)	M. p.	Solvent for recrystn.[a]
1	2,4,6,6-$(NHPr^n)_4$	Et_2O, room temp.	9	93°	Pet-1
2	$(NHPr^n)_6$	Et_2O, b. p., 3 hr.	17	59	EtOAc
3	2,4,6,6-$(NHPr^i)_4$	Et_2O, room temp.	96	126	Pet-2
4	$(NHPr^i)_6$	C_6H_6, 120°, 16 hr.[b]	34	81	Pet-1
5	$(NHBu^n)_6$	Et_2O, room temp.	23	48	Pet-1
6	$(NHBu^i)_6$	C_6H_6, 120° 12 hr.[b]	77	59	Pet-1
7	2,4,6,6-$(NHBu^s)_4$	Et_2O, room temp.	14	71	Pet-2
8	2,4,6,6-$(NHBu^t)_4$	Et_2O, room temp.[c]	95	155·5	Pet-2
9	$(Cyclohexylamino)_6$	C_6H_6, b. p., 1 hr.	17	165	Pet-2
10	$(NEt_2)_6$	C_6H_6, 150°, 24 hr.[b]	62·5	205	aq. MeOH
11	4,6-$(NBu^i_2)_2$	Et_2O, b. p., 24 hr.	8	73	Pet-1
12	4,6-$(Dicyclohexylamino)_2$	C_6H_6, b. p., 150, hr.	2	200	Pet-2
13	2,4,6-$(NBu^n_2)_3$	C_6H_6, 140°, 48 hr.[b]	42	B. p. 170/0·01.	—
14	$(p\text{-Toluidino})_4$[d]	C_6H_6, b. p., 1 hr.[e]	13·5	174	Et_2O
15	$(p\text{-Toluidino})_6$[f]	C_6H_6, b. p., 1 hr.	64	243	Pet-2
16	$(NMe_2)_6$[g]	C_6H_6, 90°, 3 hr.[b]	91	104	Pet-2
17	$(Piperidino)_6$[h]	C_6H_6, b. p., 12 hr.	19	266	EtOH

	Found (%[i])						Required (%[i])				
No.	C	H	Cl	N	*M*	Formula	C	H	Cl	N	*M*
1	33·2	7·2	16·75	23·6	—	$C_{12}H_{32}Cl_2N_7P_3$	32·9	7·4	16·2	22·4	—
2	43·9	9·95	—	26·4	479	$C_{18}H_{48}N_9P_3$	44·7	10·0	—	26·1	484
3	33·3	7·2	16·3	22·65	—	$C_{12}H_{32}Cl_2N_7P_3$	32·9	7·4	16·2	22·4	—
4	44·65	9·5	—	25·6	—	$C_{18}H_{48}N_9P_3$	44·7	10·0	—	26·1	—
5	51·4	10·9	—	22·2	567	$C_{24}H_{60}N_9P_3$	50·8	10·6	—	22·2	568
6	50·1	9·9	—	—	—	$C_{24}H_{60}N_9P_3$	50·8	10·6	—	—	—
7	38·2	8·0	14·3	19·6	—	$C_{16}H_{40}Cl_2N_7P_3$	38·8	8·15	14·3	19·8	—
8	39·3	8·1	14·3	20·8	—	$C_{16}H_{40}Cl_2N_7P_3$	38·8	8·15	14·3	19·8	—
9	59·2	9·9	—	17·4	—	$C_{36}H_{72}N_9P_3$	59·7	10·0	—	17·3	—
10	50·8	10·7	—	22·1	—	$C_{24}H_{60}N_9P_3$	50·8	10·65	—	22·1	—
11	36·7	6·8	27·1	13·4	—	$C_{16}H_{36}Cl_4N_5P_2$	36·0	6·8	26·5	13·1	—
12	45·8	7·2	20·8	10·3	—	$C_{24}H_{44}Cl_4N_5P_2$	45·2	7·0	22·2	11·0	—
13	46·1	8·5	—	—	—	$C_{24}H_{51}Cl_3N_6P_3$	46·05	8·7	—	—	—
14	—	—	11·1	15·1	—	$C_{28}H_{32}Cl_2N_7P_3$	—	—	11·25	15·6	—
15	—	—	—	16·4	—	$C_{42}H_{48}N_9P_3$	—	—	—	16·3	—
16	36·6	9·1	—	31·7	—	$C_{12}H_{36}N_9P_3$	36·45	8·2	—	31·9	—[j]

[a] Pet-1 = light petroleum of b. p. 40—60°; Pet-2 = light petroleum of b. p. 60—80°. [b] Reaction carried out in autoclave or sealed tube. [c] 12 Hr. in benzene at 140° yielded 60% of tetrasubstituted product, the remainder being an insoluble material not melting below 360°. [d] Bode, Bütow, and Lienau (*Chem. Ber.*, 1948, **81**, 547) report m. p. 174°. [e] 8 Equivalents of *p*-toluidine used. [f] Hoffmann (*Ber.*, 1884, **17**, 1909) reports m. p. 243°. [g] Becke-Goehring, John, and Fluck (*Z. anorg. Chem.*, 1959, **302**, 103) report m. p. 100°. [h] Bode *et al.*[4] report m. p. 166°. [i] Except for *M*. [j] Found: P, 23·25; calc.: P, 23·5%.

compound, m. p. 103° (1·24 g., 23%), was also obtained from the reaction of the hexachloro-compound (5 g.) in ether (60 ml.) with 30% aqueous dimethylamine.

2,4,6-*Trichloro*-2,4,6-*trisdimethylaminocyclotriphosphazatriene*.—Dimethylamine (3·7 g., 0·082 mole) was added to the hexachloro-compound (5 g., 0·0144 mole) in ether (50 ml.) at −78°, and the mixture was set aside for 18 hr., then filtered. The solid obtained from the filtrate was recrystallised from light petroleum to give flakes of 2,4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene, m. p. 104·5—105·5° (lit.,[9] m. p. 107°) (3·15 g., 58·5%) (Found: C, 19·4; H, 5·0; Cl, 29·1; N, 22·9. Calc. for $C_6H_{18}Cl_3N_6P_3$: C, 19·3; H, 4·85; Cl, 28·5; N, 22·5%).

2,4-*Dichloro*-2,4,6,6-*tetrakisdimethylaminocyclotriphosphazatriene*.—(i) Excess of dimethylamine was added to the hexachloro-compound (10 g.) in ether (75 ml.) at 0°. After the vigorous reaction further amine was added until no more amine hydrochloride was precipitated. The solid obtained by evaporation of the filtrate recrystallised from light petroleum to give 2,4-*dichloro*-2,4,6,6-*tetrakisdimethylaminocyclotriphosphazatriene*, (A) m. p. 103·5—104° (8·7 g., 79%) (Found: C, 25·8; H, 6·2; Cl, 18·1; N, 25·8. $C_8H_{24}Cl_2N_7P_3$ requires C, 25·1; H, 6·3; Cl, 18·5; N, 25·65%).

(ii) Dimethylamine (5·2 g., 0·115 mole) was added to the hexachloro-compound (5 g., 0·144 mole) in ether (150 ml.) at −78°. After 36 hr. at room temperature the amine hydrochloride

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was filtered off. Concentrating the filtrate yielded 2,4-*dichloro*-2,4,6,6-*tetradimethylaminocyclotriphosphazatriene* (B) (0·92 g., 7%), m. p. 101—101·5° (from light petroleum), mixed m. p. with (A) 71—87° (Found: C, 25·4; H, 6·1; Cl, 17·6; N, 25·0%). (This compound was observed in only one experiment.) From the mother-liquor, compound (A) (2·59 g., 45·5%) was obtained.

Attempted Preparation of Chloropentakisdimethylaminocyclotriphosphazatriene.—2,4-Dichloro-2,4,6,6-tetrakisdimethylaminocyclotriphosphazatriene (2 g., 0·0052 mole) in benzene (8 ml.) was heated in a sealed tube for 12 hr. at 90° with dimethylamine (0·5 g., 0·011 mole). After removal of dimethylamine hydrochloride (0·52 g., 0·0048 mole) and of the solvent, the solid residue was recrystallised from light petroleum to give hexadimethylaminocyclotriphosphazatriene (1·05 g., 0·0027 mole), m. p. and mixed m. p. 103—104°. The mother-liquor was chromatographed on silica gel (35 g., heated at 400° for 3 hr.). Benzene eluted starting material, m. p. and mixed m. p. 103·5° (0·63 g., 31·5%). Thus most of the amine (93%) and of the phosphazene (83·5%) were accounted for, but no pentasubstituted compound could be found.

Pentachlorodiethylaminocyclotriphosphazatriene.—Diethylamine (3·0 g., 0·041 mole) was added to the hexachloro-compound (10 g., 0·0288 mole) in ether (50 ml.). After 18 hr. the amine hydrochloride was filtered off and a colourless oil obtained from the solution. This was chromatographed on silica gel (45 g., heated at 400° for 3 hr.) with light petroleum as eluant. The first fraction was starting material (1·38 g.); the second yielded on distillation *pentachlorodiethylaminocyclotriphosphazatriene* (1·60 g., 14%), b. p. 81—83°/0·01 mm., n_D^{22} 1·5310 (Found: C, 13·2; H, 3·0; Cl, 46·5; N, 14·6. $C_4H_{10}Cl_5N_4P_3$ requires C, 12·5; H, 2·3; Cl, 46·1; N, 14·6%).

2,2,4,6-*Tetrachloro*-4,6-*bisdiethylaminocyclotriphosphazatriene.*—Diethylamine (6·5 g., 0·089 mole) was added to the hexachloro-compound (5 g., 0·0144 mole) in benzene (50 ml.) and the solution was boiled for 3 hr. The amine hydrochloride was filtered off and an orange oil obtained from the solvent. This was kept at −78° (30 hr.) and was then collected; recrystallised from light petroleum it gave 2,2,4,6-*tetrachloro*-4,6-*bisdiethylaminocyclotriphosphazatriene*, m. p. 134° (0·44 g., 7%) (Found: C, 22·3; H, 5·0; Cl, 32·9; N, 16·0. $C_8H_{20}Cl_4N_5P_3$ requires C, 22·8; H, 4·8; Cl, 33·7; N, 16·6%).

2,4,6-*Trichloro*-2,4,6-*trisdiethylaminocyclotriphosphazatriene.*—(*a*) Diethylamine (13·0 g.) and the hexachloro-compound (5 g.) in benzene (50 ml.) were boiled for 18 hr. Removal of the amine hydrochloride and evaporation yielded an orange oil which was chromatographed on silica gel (45 g., heated at 350° for 3½ hr.). Light petroleum eluted 2,4,6-*trichloro*-2,4,6-*trisdiethylaminocyclotriphosphazatriene*, b. p. 102°/2 mm., n_D^{23} 1·5100 (only one peak found in vapour-phase chromatography) (2·15 g., 33%). This product did not solidify even after 1½ years (Found: C, 31·45; H, 6·6; Cl, 22·8; N, 18·3. $C_{12}H_{30}Cl_3N_6P_3$ requires C, 31·5; H, 6·6; Cl, 23·2; N, 18·4%).

(*b*) Diethylamine (8·8 g., 0·12 mole) and the hexachloro-compound (3·5 g., 0·01 mole) in toluene (50 ml.) were boiled for 5 hr. Evaporation of the filtrate gave the above product, m. p. 162° (lit.,[10] m. p. 162°) (from light petroleum) (12%) (Found: C, 31·2; H, 6·3; N, 17·6%).

2,4-*Dichloro*-2,4,6,6-*tetrakisdiethylaminocyclotriphosphazatriene.*—The hexachloro-compound (5 g., 0·0144 mole) in benzene (25 ml.) was heated with diethylamine (8·5 g., 0·116 mole) in a sealed tube at 140° for 16 hr. After removal of the amine hydrochloride (6·8 g., 0·053 mole) and of solvent an orange oil remained, that was chromatographed in light petroleum on silica gel (45 g., heated at 450° for 3 hr.). Light petroleum eluted 2,4-*dichloro*-2,4,6,6-*tetrakisdiethylaminocyclotriphosphazatriene*, b. p. 125°/0·02 mm., n_D^{22} 1·5103 (2·2 g., 31%) (Found: C, 37·8; H, 7·5; N, 19·2. $C_{16}H_{40}N_7Cl_2P_3$ requires C, 38·9; H, 8·15; N, 19·85%).

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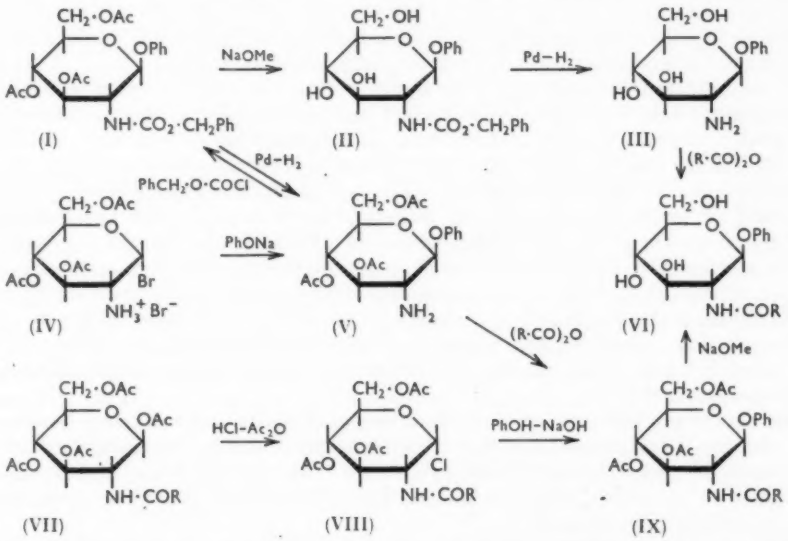
[*Received, June 3rd,* 1960.

185. *The Preparation of Phenyl 2-Amino-2-deoxy-β-D-gluco-pyranoside and Some 2-Acylamino-derivatives thereof.*

By C. G. Greig, D. H. Leaback, and P. G. Walker.

Difficulties in the preparation of phenyl 2-amino-2-deoxy-β-D-glucoside have been overcome, and syntheses of some 2-acylamino-derivatives of this compound are described.

Phenyl 2-amino-2-deoxy-β-D-glucoside (III) and some 2-acylamino-derivatives (VI) were required for studies on enzyme specificity: a preliminary account of the preparation of these compounds has appeared.[1] The preparation of phenyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucoside (V) by the condensation of 3,4,6-tri-*O*-acetyl-2-amino-1-bromo-2-deoxy-α-D-glucose hydrobromide [2] (IV) with sodium phenoxide has been described [3] but difficulties with the method have been reported.[4] In our hands, the published method [3]



gave extremely low yields of a product of poor quality; a modification [5] gave better yields of the glycoside (V) but difficulties were encountered in its purification and deacetylation. These difficulties were overcome by condensing the crude product with benzyl chloroformate, to give a highly crystalline derivative (I) which, on deacetylation and hydrogenolysis, gave the required amino-compound (III) with a higher melting point than that reported.[3] Overall yields were low but reproducible. The amino-compound (III) was converted into the known acetamido-derivative (VI; R = Me) by the method of Roseman and Ludowieg.[6] Preliminary experiments on the preparation of the amino-compound (V) through *N*-phthaloyl [7] or *N*-dinitrophenyl [8] derivatives of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose [9] were unpromising. Acylamino-compounds of the type (IX) can be

[1] Greig and Leaback, *Chem. and Ind.*, 1960, 376.
[2] Irvine, McNicoll, and Hynd, *J.*, 1911, **99**, 250.
[3] Helferich, Iloff, and Streech, *Z. physiol. Chem.*, 1934, **226**, 258.
[4] Roseman and Dorfman, *J. Biol. Chem.*, 1951, **191**, 607.
[5] Cf. May and Mossetig, *J. Org. Chem.*, 1950, **15**, 890.
[6] Roseman and Ludowieg, *J. Amer. Chem. Soc.*, 1954, **76**, 301.
[7] Baker, Joseph, Schaub, and Willams, *J. Org. Chem.*, 1954, **19**, 1786.
[8] Lloyd and Stacey, *Chem. and Ind.*, 1956, 917.
[9] Bergman and Zervas, *Ber.*, 1931, **64**, 979.

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obtained by acylation of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose hydrochloride, followed by chlorination of the resulting tetra-acetate (VII) and condensation of the chloro-sugar (VIII) with sodium phenoxide;[10] the propionamido- (IX; R = Et) and the monofluoroacetamido-derivative (IX; R = CH_2F) were prepared by this route as well as by way of the amino-compound (V).

Attempts to prepare a chloro-sugar from 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-formamido-β-D-glucose (VII; R = H) led to syrups; the failure was probably due to the acid lability of the formamido-group[11] and suggests that compounds of the type (IX) with acid-labile acylamino-groups can only be prepared by acylation of the amino-compound (V). The formamido-derivative (IX; R = H) was prepared from the amino-compound (V) by using acetic anhydride in formic acid[11] and was deacetylated to phenyl 2-deoxy-2-formamido-β-D-glucoside (VI; R = H).

Dicyclohexylcarbodi-imide has been used in the synthesis of peptide bonds[12] and we have examined its use for synthesis of compounds of the type (IX); we thus prepared the monofluoroacetamido-derivatives of the tetra-acetate (VII) and the acetylated phenyl glycoside (V); although yields were not high, this method should find application (as in this instance) when the appropriate acid anhydride is not available.

Fodor and Ötvös[13] reported that the optical rotation of a solution of ethyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucose [an alkyl analogue of (V)] in dry acetone changed with time, and that ethyl 2-acetamido-4,6-di-O-acetyl-2-deoxy-β-D-glucose could then be isolated. In the present work, it was important to establish whether the amino-compound (V) underwent a similar transformation. The optical rotation of solutions of the amino-compound (V) in dry acetone remained unchanged for 72 hours at room temperature, and the infrared spectra of the pure amino-compound (II) and of the material recovered from acetone solution were identical and showed no signs of the presence of an acetamido-group. It was concluded that, unlike the corresponding ethyl glycoside, under these conditions the phenyl glycoside (II) was unable to assume a conformation which favoured the *O*- ⟶ *N*-acetyl migration. However, such transformations under strongly basic conditions are well established[14,15] and might account for difficulties[16] in the direct deacetylation of the amino-compound (V).

The nature and homogeneity of preparations of phenyl 2-amino-2-deoxy-β-D-glucoside (III) and the 2-acylamino-derivatives (VI) were confirmed by the behaviour of these compounds on paper chromatograms (see Table). As expected,[17] the amino-compound (III) gave an elongated spot, but the acylamino-derivatives (VI) gave single discrete spots in both the solvents used.

With one exception,[15] the reported reactions of the bromo-sugar (IV) proceeded with inversion at position 1. Since the 2-substituent is known[18] to influence the steric course of reactions of acetohalogeno-sugars at position 1, we investigated the degree with which the bromo-sugar (IV) reacted with inversion under our conditions, taking advantage of a solvent (see Table) which gave a clear separation of the anomeric phenyl 2-acetamido-2-deoxy-D-glucosides on paper chromatograms. The crude products of a condensation of the bromo-sugar (IV) with sodium phenoxide were *N*-acetylated and catalytically de-*O*-acetylated to give chromatographically pure phenyl 2-acetamido-2-deoxy-β-D-glucoside (III; R = Me): control experiments indicate that the procedure would have detected the presence of 5% of the α-anomer in the preparation. It was concluded that this reaction

[10] Leaback and Walker, *J.*, 1957, 4754.
[11] Sheehan and Jang, *J. Amer. Chem. Soc.*, 1958, **80**, 1154.
[12] Sheehan and Hess, *J. Amer. Chem. Soc.*, 1955, **77**, 1076.
[13] Fodor and Ötvös, *Chem. Ber.*, 1956, **89**, 701.
[14] White, *J.*, 1938, 1498.
[15] Maley, Maley, and Lardy, *J. Amer. Chem. Soc.*, 1956, **78**, 5303.
[16] Greig and Leaback, unpublished work.
[17] Cf. Leaback and Walker, *Biochem. J.*, 1957, **67**, 22P.
[18] Lemieux, *Adv. Carbohydrate Chem.*, 1954, **9**, 1.

proceeded with a high degree of inversion: this result is similar to that found with the anomeric 3,4,6-tri-*O*-acetyl-1-chloro-D-glucose compounds.[19]

Experimental

Paper chromatography was carried out on Whatman No. 1 paper by the descending method with the non-polar phase of (*a*) butan-1-ol–ethanol–water (4 : 1 : 5; v/v) or (*b*) isopropyl ether–ethanol–water (2 : 1 : 1; v/v), and the separate substances were detected by a modification [20] of Rydon and Smith's method.[21] R_F values were as tabulated.

Except for compound (II), materials were dried for 16 hr. at 100° (over P_2O_5) before analysis. Solutions were evaporated under reduced pressure.

Phenyl 3,4,6-*Tri*-O-*acetyl*-2-*amino*-2-*deoxy*-β-D-*glucoside* (V).—Sodium (1·1 g.) was dissolved in a solution of phenol (11 g.) in dry acetone (50 ml.), and the mixture was added to crystalline 3,4,6-tri-*O*-acetyl-2-amino-1-bromo-2-deoxy-α-D-glucose hydrobromide (I) (11 g.) in dry acetone (100 ml.). The mixture was left for 16 hr. at room temperature, and the precipitated sodium bromide filtered off. The filtrate was evaporated to a brown oil, which was mixed with water (200 ml.) and left for 16 hr. at 5°. The brown solid was filtered off and dried *in vacuo* to give the crude phenyl glycoside (V) (9 g.). No solvent suitable for recrystallisation was found.

Compound	R_F (solvent *a*)	R_F (solvent *b*; relative to compound VI; R = Me)
III	0·46—0·58	0·62
VI; R = H	0·62	0·91
VI; R = Me	0·67	1·00
VI; R = CH_2F ...	0·69	1·28
VI; R = Et	0·78	1·40
α-Anomer of (VI; R = Me)	0·69	1·36

The crude glycoside (V) (2 g.) was treated for 16 hr. at room temperature with acetic anhydride (5 ml.) and pyridine (20 ml.). Chloroform (100 ml.) was added and the solution extracted successively with water, dilute hydrochloric acid, water, saturated sodium hydrogen carbonate, and water, before it was dried and evaporated to leave a brown residue. Dry methanol (10 ml.) and N-sodium methoxide (1 ml.) were added and the solution left for 24 hr. at 5° before evaporation to dryness: on paper chromatograms (solvent *b*), the crude residue showed the presence of only phenyl 2-acetamido-2-deoxy-β-D-glucoside.

The pure phenyl glycoside (V) was obtained by hydrogenation of phenyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucoside (I) (1 g.) in methanol (270 ml.) in the presence of 5% palladium–charcoal (0·5 g.). After the hydrogen uptake was complete (2½ hr.), the catalyst was filtered off and the filtrate evaporated to give phenyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucoside (II) (0·6 g., 81%) which was recrystallised from ethyl acetate–light petroleum to give a product, m. p. 158—160° (decomp.), $[\alpha]_D^{21}$ −45° (*c* 1 in acetone) (Found: C, 56·7; H, 6·2; N, 3·8. $C_{18}H_{23}NO_8$ requires C, 56·7; H, 6·0; N, 3·7%). The infrared spectrum (KCl pellet) showed large bands at 3100 (NH) and 1740 cm.$^{-1}$ (O·CO) but no absorption (in the 1650—1550 cm.$^{-1}$ region) attributable to a secondary amide. The infrared spectrum and optical rotation of this compound were unchanged after its dissolution for 72 hr. in dry acetone.

Phenyl 3,4,6-*Tri*-O-*acetyl*-2-*benzyloxycarbonylamino*-2-*deoxy*-β-D-*glucoside* (I).—The crude glycoside (V) (9 g.) was dissolved in acetone (216 ml.) and water (54 ml.); sodium hydrogen carbonate (1·95 g.) and benzyl chloroformate (3·15 ml.) were added with shaking, the mixture left for 16 hr. at room temperature, then filtered and evaporated at 37°. The brown residue was washed with ether and recrystallised from ethanol to give the *derivative* (I) (3·2 g., 27%), m. p. 186—187°, $[\alpha]_D^{19}$ +5·9° (*c* 1 in $CHCl_3$) (Found: C, 60·6; H, 6·1; N, 2·8. $C_{26}H_{29}NO_{10}$ requires C, 60·6; H, 5·6; N, 2·7%).

Phenyl 2-*Benzyloxycarbonylamino*-2-*deoxy*-β-D-*glucoside* (II).—Phenyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucoside (3 g.) was suspended in dry methanol (15 ml.),

[19] Lemieux and Huber, *Canad. J. Chem.*, 1955, **33**, 128.
[20] Greig and Leaback, *Nature*, 1960, **188**, 310.
[21] Rydon and Smith, *Nature*, 1952, **169**, 922.

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N-sodium methoxide (3 ml.) added, the suspension shaken gently for 15 min., and the solution left for 16 hr. at 5°. The solid material was filtered off and recrystallised from water, to give the de-acetylated glycoside (II) (1·7 g., 75%), m. p. 209—211°, $[\alpha]_D^{24}$ −10·7° (*c* 1 in MeOH) (Found: C, 59·1; H, 6·2; N, 3·5. $C_{20}H_{23}NO_7,H_2O$ requires C, 59·0; H, 6·2; N, 3·4%).

Phenyl 2-Amino-2-deoxy-β-D-glucoside (III).—Phenyl 2-benzyloxycarbonylamino-2-deoxy-β-D-glucoside (2·3 g.) was hydrogenated in methanol (225 ml.) in the presence of 5% palladium–charcoal (0·5 g.) (2½ hr.). The catalyst was filtered off and the filtrate evaporated. The residue recrystallised from ethanol to give the phenyl glycoside (III) (1·2 g., 80%), m. p. 174—175° (lit.,[3] 167·5—170°), $[\alpha]_D^{20}$ −77·5° (*c* 0·6 in H_2O) (Found: C, 56·1; H, 6·7; N, 5·6. Calc. for $C_{13}H_{17}NO_5$: C, 56·5; H, 6·7; N, 5·5%). The compound gave a positive ninhydrin reaction on paper chromatograms.

Phenyl 2-Acetamido-2-deoxy-β-D-glucoside (VI; R = Me).—Phenyl 2-amino-2-deoxy-β-D-glucoside (0·9 g.) in water (100 ml.) and methanol (10 ml.) was stirred in ice with the carbonate form of Deacidite FF resin (27 ml.). Acetic anhydride (0·5 ml.) was added and the mixture stirred for 90 min. before the resin was filtered off and the filtrate passed through a column (20 × 1·5 cm.) of IR-100 resin (H^+). The eluate was evaporated to a residue which recrystallised from water to give phenyl 2-acetamido-2-deoxy-β-D-glucose (0·36 g., 35%) identical in m. p., mixed m. p., and optical rotation with an authentic sample.[10]

Phenyl 3,4,6-Tri-O-acetyl-2-deoxy-2-formamido-β-D-glucoside (IX; R = H).—Crude phenyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucoside (12 g.) was dissolved in 90% formic acid (78 ml.), and acetic anhydride (32 ml.) was added at a rate which kept the temperature of the solution at 50—60°; the solution was maintained for 1 hr. at this temperature and then set aside for 16 hr. Chloroform (200 ml.) was added, and the solution extracted successively with water, cold saturated sodium hydrogen carbonate solution, water, dilute hydrochloric acid, and water. The chloroform layer was dried ($MgSO_4$), decolorised (charcoal), and evaporated, and the residue recrystallised from ethanol to give the *formamido-compound* (1·0 g., 8%) (IX; R = H), m. p. 187—188°, $[\alpha]_D^{24}$ −29° (*c* 0·5 in $CHCl_3$) (Found: C, 56·3; H, 5·5; N, 3·2. $C_{19}H_{23}NO_9$ requires C, 55·8; H, 5·6; N, 3·4%).

Phenyl 2-Formamido-2-deoxy-β-D-glucoside (VI; R = H).—Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-formamido-β-D-glucoside (0·98 g.) was suspended in dry methanol (5 ml.), and N-sodium methoxide (1 ml.) was added with swirling. After 24 hr. at 5°, the solid was filtered off and recrystallised from water, to give the deacetylated *glycoside* (VI; R = H) (0·6 g., 89%), m. p. 203—204°, $[\alpha]_D^{20}$ −13·7° (*c* 0·6 in H_2O) (Found: C, 54·3; H, 6·0; N, 4·9. $C_{13}H_{17}NO_6$ requires C, 55·1; H, 6·0; N, 4·9%).

1,3,4,6-*Tetra*-O-*acetyl*-2-*deoxy*-2-*formamido*-β-D-*glucose* (VII; R = H).—Crude 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose [9] (2 g.) was dissolved in 90% formic acid (20 ml.), and acetic anhydride (4·9 ml.) added with stirring. The mixture was kept at 50—60° for 1 hr. and the whole left at room temperature for 16 hr. Chloroform (100 ml.) was then added. Working up as above gave the *formamido-compound* (0·7 g., 33%), m. p. 191—192°, $[\alpha]_D^{23}$ +2·5° (*c*, 1 in $CHCl_3$) (Found: C, 48·8; H, 5·9; N, 3·7. $C_{15}H_{21}NO_{10}$ requires C, 48·0; H, 5·6; N, 3·7%). Attempts to prepare the chloro-sugar (VIII; R = H) from the formamido-compound led to syrups.

1,3,4,6-*Tetra*-O-*acetyl*-2-*deoxy*-2-*propionamido*-β-D-*glucose* (VII; R = Et).—To a suspension of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose hydrochloride [9] (30 g.) in chloroform (200 ml.) was added sodium carbonate (9·5 g.) in water (100 ml.). The mixture was stirred until dissolution was complete, propionic anhydride (40 ml.) added, and stirring continued for 30 min. The chloroform layer was extracted successively with water, cold aqueous sodium hydrogen carbonate, water, dilute hydrochloric acid, and water. The dried chloroform layer was evaporated and the residue recrystallised from ethanol to give the *propionamide* (19 g., 47%), m. p. 174—176°, $[\alpha]_D^{20}$ −4·2° (*c* 0·9 in $CHCl_3$) (Found: C, 50·6; H, 6·1; N, 3·5. $C_{17}H_{25}NO_{10}$ requires C, 50·6; H, 6·2; N, 3·4%).

The butyramide tetra-acetate (VII; R = Pr^n), prepared similarly in 55% yield, had m. p. 168—170°, $[\alpha]_D^{20}$ −4·5° (*c* 1 in $CHCl_3$).

Phenyl 2-Deoxy-2-propionamido-β-D-glucoside (VI; R = Et).—1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-propionamido-β-D-glucose (21 g.) was dissolved in acetic anhydride (60 ml.), saturated at 0° with dry hydrogen chloride, and left for 16 hr. Chloroform (200 ml.) was added, and the solution extracted with cold water, aqueous $NaHCO_3$, and water. The chloroform layer was dried ($MgSO_4$) and evaporated to dryness to yield the chloro-sugar (VIII; R = Et)

(13·1 g.), m. p. 122—124°, $[\alpha]_D^{20}$ +132·5° (*c* 1 in acetone). This was left with phenol (4·1 g.) in acetone (90 ml.) and N-sodium hydroxide (35 ml.) for 16 hr. at room temperature, the acetone then evaporated at room temperature, and chloroform (300 ml.) added to the residue. The chloroform layer was extracted successively with water, aqueous sodium hydroxide, and water, dried ($MgSO_4$), and evaporated, to give the glycoside (IX; R = Et) (3·6 g.), m. p. 194—195°, $[\alpha]_D^{20}$ −22·4° (*c* 0·6 in acetone).

This glycoside (2·5 g.) was suspended in dry methanol (25 ml.), and N-sodium methoxide (2·5 ml.) added with shaking. After 16 hr. at 5° the solid was filtered off and recrystallised from water to give *phenyl 2-deoxy-2-propionamido-β-D-glucoside* (1·4 g.), m. p. 237—238°, $[\alpha]_D^{18}$ −8·3° (*c* 0·6 in H_2O) (Found: C, 57·5; H, 6·6; N, 4·3. $C_{15}H_{21}NO_6$ requires C, 57·9; H, 6·8; N, 4·5%).

Phenyl 2-Deoxy-2-fluoroacetamido-β-D-glucoside (VI; R = CH_2F).—(i) The pure amino-compound (V) (1·7 g.) and dicyclohexylcarbodi-imide (0·8 g.) were dissolved in a cooled mixture of dry chloroform (40 ml.) and pyridine (3·2 ml.). Monofluoroacetic acid (0·7 ml.) was added with shaking and the mixture left for 16 hr. at 5°. The solid was filtered off and the filtrate washed with water, dilute hydrochloric acid, and water. The chloroform layer was dried and evaporated, to leave a solid which recrystallised from ethanol to give phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoroacetamido-β-D-glucoside (0·52 g., 27%), m. p. 186—188°, $[\alpha]_D^{19}$ −18·5° (*c* 1 in MeOH).

The fluoroacetamide (0·5 g.) was dissolved in dry methanol (5 ml.) containing N-sodium methoxide (0·5 ml.) and left for 16 hr. at room temperature. The solid was filtered off and recrystallised from water to give phenyl 2-deoxy-2-fluoroacetamido-β-D-glucoside (0·3 g., 84%), m. p. 242—245°, $[\alpha]_D^{20}$ −14·0° (*c* 0·5 in H_2O) (Found: C, 54·0; H, 5·9; N, 4·3. $C_{14}H_{18}FNO_6$ requires C, 53·3; H, 5·7; N, 4·4%).

(ii) 1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose [9] (8 g.) and dicyclohexylcarbodi-imide (3·9 g.) were left in chloroform (100 ml.), pyridine (15·8 ml.), and monofluoroacetic acid (3·4 ml.) at 5° for 16 hr. before the solid was filtered off and the chloroform layer washed as above and evaporated to a residue which recrystallised from ethanol to yield 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-fluoroacetamido-β-D-glucose (VII; R = CH_2F) (4·2 g., 50%), m. p. 176—179°, $[\alpha]_D^{20}$ −5·4° (*c* 1 in $CHCl_3$). This was converted (cf. the propionamide) into the chloro-sugar (VIII; R = CH_2F) and condensed with phenol, and the resultant glycoside was deacetylated; this gave material (VI; R = CH_2F) (0·3 g., overall yield 9%) identical in optical rotation, m. p., and mixed m. p. with that prepared as under (i).

The authors are indebted to Dr. R. K. Callow for measurement of infrared spectra, and to the Medical Research Council and the Nuffield Foundation for grants.

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186. *The Oxidation of Calcium in Moist Oxygen.*

By S. J. Gregg and W. B. Jepson.

The oxidation of calcium in moist oxygen corresponding to saturation with water at 0° and 25° has been studied by a thermal-balance technique at temperatures in the ranges 200—400° and 50—525°, respectively. It is shown that the reaction is between calcium and water vapour, the oxygen acting as a carrier gas; at temperatures above 200° the reaction is $Ca + H_2O = CaO + H_2$, followed by $CaO + H_2O = Ca(OH)_2$ when all the metal has been oxidised. The product formed below 200° is white, whereas that formed at the higher temperatures is green. This coloration is ascribed to the presence of calcium hydride.

The rate of oxidation is shown to *decrease* with increasing temperature over the ranges 50—150°, 250—300°, and 425—525°, and to increase with increasing temperature in the ranges 200—250° and 325—375°. At 425° and above, " breakaway " occurs. The kinetic results are in broad accord with those of other workers for the oxidation of calcium in water vapour.

The reaction mechanism is discussed.

The kinetics of the oxidation of calcium in dry oxygen was the subject of a recent paper [1] (hereafter referred to as Part I), and in the present paper the study has been extended to moist oxygen, a field which has hitherto received but little attention. The ranges 200—400° and 50—525° have been investigated with oxygen saturated with water vapour at 0° and 25°, respectively.

The results obtained indicate that the reaction occurs with the water vapour alone, the oxygen merely acting as a carrier gas.

Experimental

Materials.—The calcium (stated to be 99·95% pure, excluding magnesium the content of which was 0·5% maximum) was part of the same batch as was used in the earlier paper,[1] and the surface was again prepared by filing.

Method.—The weight gain of the sample as a function of time was determined gravimetrically by means of a thermal balance.[2] Two humidities of oxygen were used, corresponding to saturation with water vapour at 25° (mixture A) and at 0° (mixture B), the saturation pressures being 23·8 and 4·58 mm., respectively. One set of experiments was carried out with argon in place of oxygen, and a water content corresponding to saturation at 25° (mixture C, 23·8 mm. saturation pressure).

Results.—(a) *Kinetics.* The curves for mixture A at temperatures in the range 50—525° are given in Figs. 1—4. They clearly do not conform to a simple pattern, and the gain of weight after a given time does not increase uniformly with increase in temperature, but actually decreases between 50° and 150° (Fig. 1), between 250° and 300° (Fig. 2), and between 425° and 525° (Fig. 4). The curves fall into three groups: (i) where the rate of oxidation continuously decreases along branch OA (cf. 50°, Fig. 1) to reach a constant or nearly constant rate along AB; (ii) where the rate *increases* along OA (cf. 250°, Fig. 2) to a constant rate along AB; (iii) where the rate first decreases until at P (cf. 425°, Fig. 4) it increases fairly rapidly in the manner characteristic of " breakaway." The Table summarises the type of curve and the average linear rate for each temperature; it will be noted that at 425° and above, the curves are exclusively of Group (iii). The linear rate of Groups (i) and (ii) in duplicate runs at a given temperature agreed within ±10%; in the Group (iii) the weight gains at a given temperature again agreed within ±10%, except at 525° where the onset of breakaway varied, in different runs, between 6 and 20 hr. (Fig. 4).

Although a linear branch, corresponding to a constant rate of oxidation, was a characteristic feature of the curves of Groups (i) and (ii), it does not follow that the metal would

[1] Gregg and Jepson, *J.*, 1960, 712.
[2] Gregg and Jepson, *J. Inst. Metals*, 1958—59, **87**, 187.

FIG. 1. *Oxidation of calcium in moist oxygen (mixture A) at 50—150°. (Curve OD is calculated from the data of Svec and Apel [6] and is referred to in the text.)*

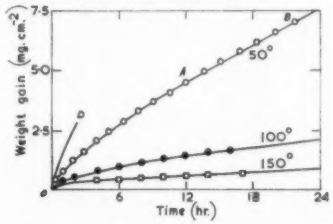


FIG. 2. *Oxidation of calcium in moist oxygen (mixture A) at 150—375°.*

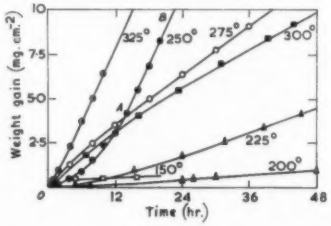


FIG. 3. *Oxidation of calcium in moist oxygen (mixture A) at 325—400°.*

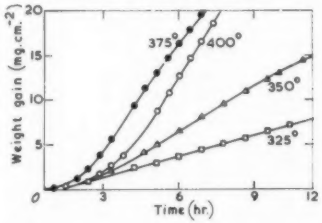


FIG. 4. *Oxidation of calcium in moist oxygen (mixture A) at 400—*

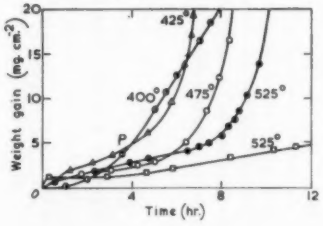


FIG. 5. *Oxidation of calcium in moist oxygen (mixture A) at 250—250°. The weight gain is now plotted as the specific weight gain (g./g. of initial metal) and not as mg./cm.² as in Figs. 1—4. The curves for 300° and 350° accidentally coincide: the initial area of metal was not the same in each run. The specific weight gains corresponding to conversion into oxide and into hydroxide are 0·4 and 0·85 g./g., respectively.*

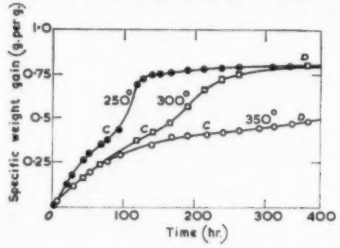
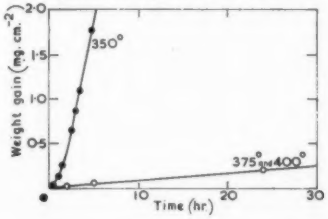


FIG. 6. *Oxidation of calcium in moist oxygen (mixture B) at 350—400°.*



continue to oxidise to completion at this rate. Thus in the 400-hr. runs at 250°, 300°, and 350° (Fig. 5) the linear branch ended at about 20 hr. and was succeeded by a curve of variable slope.

In mixture B the experiments were confined to the temperature range 200—500°. For temperatures up to and including 350° the curves closely resembled those for mixture A except that the linear rate was smaller (Table); but at 375° and 400° there were marked differences between the two mixtures; the results for these two temperatures now fell on the *same* curve, which lay much below that for 350° (contrast Figs. 6 and 3).

Runs carried out at six representative temperatures between 50° and 425°, with argon in place of oxygen (mixture C), gave curves agreeing within experimental error with those obtained by using the oxygen mixture of the same humidity (mixture A) at the same temperatures, and the appearance of the samples at the end of the run was similar; moreover, in a blank test using dry argon alone at 525°, the weight gain in 24 hr. was only 0·25 mg./cm.^{2}. It seems clear, therefore, that the oxygen functions merely as a carrier gas.

(b) *Reaction product.* At all temperatures the reaction product remained adherent to the metal during the run itself, but fragments of it spalled on cooling from heavily oxidised specimens. The specific surface areas of the products prepared at 50°, 100°, and 350°, as measured by the method of krypton sorption,[4] were 41, 18, and >100 m.^{2} g.$^{-1}$, respectively.

With all three mixtures the colour of the product varied according to the temperature of the experiment: at 50° it was a white layer (hydroxide), and 100° and 150° it was light grey with traces of white; at 200° and above it had a colour which varied from dark green at 250° to khaki at 350°; and at 425° and above it was straw-coloured with patches of green.

Now, in Part I, the oxide obtained in dry oxygen also had a green colour which was assumed to be due to the excess of calcium thought to be present. It seems reasonable, however, to suppose that the constituent responsible for the colour is common to oxides prepared both in dry and in moist oxygen; and it is now suggested that this constituent is calcium hydride. The presence of this substance has already been demonstrated [3] in the product from calcium oxidised in pure water vapour at 177—369°; and its content was determined [1] directly in the products obtained at 300° and above (Table) by chipping off samples of the oxide and measuring the volume of hydrogen evolved on treatment with water. The source of the hydride present in the product formed in dry oxygen could be hydrogen dissolved in the metal.

Sections of a number of samples which had been oxidised at 300—350° indicated that the metal was completely oxidised as soon as the specific weight gain reached 0·40 g. per g., which is the calculated value for the completion of the reaction

$$Ca + H_2O = CaO + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It seems clear, therefore, that branch *OC* of the curves in Fig. 5 corresponds to reaction (1) which is complete at *C*, and branch *CD* to the hydration of the oxide

$$CaO + H_2O = Ca(OH)_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which did not, however, proceed to completion (*i.e.*, specific weight gain of 0·85 g. per g.) in the time of the experiments. Associated with this hydration is the reaction of the calcium hydride with water vapour, for the green colour of the oxide was found to persist only so long as some metal remained unoxidised: thus, samples oxidised at 350° to a specific weight gain of 0·45 appeared white although sections revealed some green coloration within the sample.

Samples oxidised in mixture B were similar in appearance to those oxidised in mixture A, except that the oxide was paler for a given temperature. It was not possible to obtain sufficient oxide for a determination of the calcium hydride content.

Discussion

Taken as a whole, the results are surprisingly complex; the curves show a variety of form and there are three ranges in which the rate of oxidation decreases with increase in temperature, *viz.*, 50—150°, 250—300°, and 425—525°. Although it is not uncommon in studies of the oxidation of metals to encounter a single range of temperature over which

[3] Gibbs and Svec, *J. Amer. Chem. Soc.*, 1953, **75**, 6053.
[4] Smith, Ph.D. Thesis, Exeter, 1958.

the reaction rate has a negative temperature coefficient,[1,5,6] yet it is unusual to find three such temperature ranges with one metal, as in the present system.

Although some fairly definite conclusions can be drawn as to the nature of the overall reaction at most of the temperatures, it is not yet possible to explain the curves in detail. One can do little more than indicate the kind of factors involved and suggest how they might influence the reactions.

The present results establish that when calcium is oxidised in moist oxygen, only the water vapour reacts and the oxygen thus functions as an inert carrier gas. Svec and Apel [6] (Fig. 1, curve *OD*) have already shown that, at temperatures in the range 20—70°, calcium reacts with water vapour according to

$$Ca + 2H_2O = Ca(OH)_2 + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and in view of the similarity both in the form of the curves and in the appearance of the samples for 50°, 100°, and 150°, there is little doubt that equation (3) also represents the reaction at 100° and 150°.

At temperatures in the range 250—350°, on the other hand, no calcium hydroxide appears in the product until all the calcium has been consumed; conversion into hydroxide then begins, and proceeds at a rate which decreases with increase in temperature (Fig. 5). The reaction sequence is thus (1) followed by (2). At temperatures above that at which the dissociation pressure of calcium hydroxide exceeds the partial pressure of water vapour in the mixture (373° for mixture A [7]), the hydration stage (2) will be absent and the product will be oxide, with possibly a monolayer of chemisorbed water on its surface.

Calcium hydride was not the main product at any temperature, its content never exceeding second-order proportions (Table). This is in contrast with Gibbs and Svec's conclusion [3] that, in water vapour at 23·8 mm. and at temperatures in the range 177—369° (later amended to 330—400° [8]), the reaction is exclusively

$$2Ca + H_2O = CaO + CaH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Oxidation of calcium in moist oxygen.

Temp.	Type of curve	Linear rate (mg./cm.²/hr.) Mixture A	Mixture B	CaH_2 content of scale formed in mixture A (mg./g.)	Temp.	Type of curve	Linear rate (mg./cm.²/hr.) Mixture A	Mixture B	CaH_2 content of scale formed in mixture A (mg./g.)
50°	I	0·248	—	—	325°	II	0·673	—	8·2
100	I	0·068	—	—	350	II	1·78	0·73	—
150	I	0·022	—	—	375	II	(3·89)	—	7·1
200	II	—	—	—	400	II	(4·11)	—	6·9
225	II	0·129	0·045	—	425	III	—	—	4·4
250	II	0·687	0·200	—	475	III	—	—	$1·1_9$
275	I	0·213	0·050	—	525	III	—	—	$1·0_4$
300	I	0·166	0·065	8·8					

as long as any calcium remains unoxidised. In the present study, one run at 350° was stopped when the weight gain was that corresponding to completion of reaction (4), *viz.*, 0·23 g. per g., yet an appreciable amount of unconsumed metal could be seen in the sectioned sample.

Attempts to fit equations to the curves were unsuccessful; this was true even at 50°, which lies within the range of temperatures (20—70°) where, according to Svec and Apel,[6] the logarithmic law

$$w = k \log (1 + ct) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

[5] Bridges and Fassell, *J. Electrochem. Soc.*, 1956, **103**, 326; Aylmore, Gregg, and Jepson, *ibid.*, 1960, **107**, 495; Hopkinson, *ibid.*, 1959, **106**, 102.
[6] Svec and Apel, *J. Electrochem. Soc.*, 1957, **104**, 346.
[7] Tamaru and Siomi, *Z. phys. Chem.*, 1932, *A*, **161**, 421.
[8] Svec and Staley, *J. Electrochem. Soc.*, 1958, **105**, 121.

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holds for calcium in water vapour (w is the weight gain at time t, and k and c are constants). It is interesting that these workers also found a negative temperature coefficient for k with an " energy of activation " (calculated from the Arrhenius plot) of $-7{\cdot}5$ kcal. mole^{-1} as compared with $-6{\cdot}6$ kcal. mole^{-1} calculated from the linear rates at 50°, 100°, and 150° of the Table.

The relatively high values of the specific surface of the product show it to be porous to water vapour; the conventional picture [2] of an oxide scale which cracks and becomes porous to the gaseous reactant, leaving a thin film (barrier film) adhering to the metal, therefore seems applicable. The reaction then proceeds by diffusion of Ca^{2+} ions and their electrons across this film to meet the water adsorbed at its outer surface (Fig. 7).

The overall rate of reaction at any one temperature will then be determined by the slowest of the following three processes: (1) the diffusion of Ca^{2+} ions across the barrier film; (2) the adsorption (physical or chemical) of water molecules at the film–gas interface;

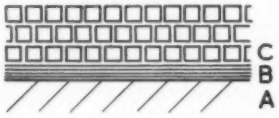

FIG. 7. *Showing the cross-section of specimen during non-protective oxidation.* (A) *Metallic calcium*; (B) *barrier film of oxide or hydroxide*; (C) *porous, outer scale.*

(3) the reaction between Ca^{2+} ions and water at the film–gas interface. With regard to process (1), the rate of diffusion of Ca^{2+} ions across the barrier film will depend upon two factors: (i) the thickness of the film itself (the thinner the film, the greater the rate of diffusion) which will depend upon the rate of cracking; [2] (ii) the concentration of imperfections in the barrier film. These imperfections could arise from the dissolution of impurities from the metal in the oxide and also from the presence of hydroxyl and carbonate ions in an oxide lattice or of oxide and hydroxyl ions in a carbonate lattice. (The freshly prepared metal surface rapidly tarnishes in air.)

Now each of the processes (1), (2), and (3) will have its own temperature coefficient and each of the factors (i) and (ii) will separately depend upon temperature; and it is clear, therefore, that the kinetics of the overall reaction could vary in a complex manner with temperature. In the absence of further data, however, it does not seem possible to provide a more detailed explanation of the experimental dependence of kinetics on temperature.

There was one rather curious feature of the results: the oxide fails to hydrate until all the metal has been consumed, despite the fact that the scale is exposed to water vapour and is highly porous. The water molecules must therefore proceed preferentially to the film–gas interface rather than to the oxide–hydroxide interface. Presumably the water molecules migrate over the surface of the oxide particles composing the scale to reach the surface of the barrier film where they react; a concentration gradient of adsorbed water molecules is thus set up and persists so long as calcium remains. If the rate of migration and of reaction is greater than the rate of hydration, the facts are explained.

We are grateful to the U.K. Atomic Energy Authority for their support of this work.

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THE UNIVERSITY, EXETER.

[*Received, August 4th*, 1960.]

187. *The Structure of the Antimycin-A Complex.*

By A. J. Birch, D. W. Cameron, Y. Harada, and R. W. Rickards.

On the basis of degradative evidence, structure (I) is proposed for the antibiotic complex antimycin-A, produced by *Streptomyces kitazawaensis*. The individual components of the complex differ in the nature of the alkyl (R = n-C_4H_9, n-C_6H_{13}) and acyl (R′ = CHMeEt, CH_2·$CHMe_2$, $CHMe_2$) substituents present. A preliminary account [1] of this work has been published.

Antimycin-A, the antibiotic responsible for the antifungal activity of certain *Streptomyces* species, was first isolated crystalline in 1949 from an unidentified *Streptomycete*.[2] Although apparently of no medical importance the substance has proved to have considerable biochemical use in connection with electron-transport processes because of its specific inhibitory action on certain of the enzymes involved.[3,4] Analytical figures and melting points of the antibiotic varied with the source and the method of purification, and the suggestion that antimycin-A was a mixture of chemically closely related substances was verified by paper-chromatographic resolution into at least four components.[4] More recently,[5] counter-current distribution has separated at least three definite components: the major constituent, antimycin-A_1, $C_{28}H_{40}O_9N_2$, the isomeric antimycin-A_2, and antimycin-A_3, $C_{26}H_{36}O_9N_2$. Blastmycin, $C_{26}H_{36}O_9N_2$, isolated by Japanese workers from *S. blastmyceticus*,[6] resembled the antimycins in its chemical properties, and more specifically antimycin-A_3 in its physical properties.[7]

In a preliminary communication [1] we advanced the structure (I; R = n-C_4H_9, n-C_6H_{13}; R′ = CHMeEt, CH_2·$CHMe_2$, or $CHMe_2$) for the antimycin-A complex. We here describe the evidence leading to this formula and confirming the identity of blastmycin with antimycin-A_3. Strong, van Tamelen, and their co-workers [8] have independently presented evidence supporting structure (I).

Very mild treatment of antimycin-A with aqueous alkali at room temperature yielded [9,10] a neutral fragment $C_{16}H_{28}O_4$, formic acid, and antimycic acid, $C_{11}H_{14}O_5N_2$, for which the proposed structure [11] (II) was confirmed by synthesis.[12] Since the antibiotic contained a free phenolic hydroxyl group and was non-basic, the presence of an *N*-formyl group was inferred.[9]

We examined this question by reduction of antimycin-A with a quantity of lithium aluminium hydride insufficient for complete reduction of the carbonyl functions present [3 mol.; structure (I) requires 3·25 mol.], wishing to reduce selectively the ester and formanilide groupings in preference to the salicylamide, which could then be hydrolysed to yield the methylaminosalicylic acid. There is some evidence [13] that esters can be selectively reduced in the presence of amides, but the preferential reduction of different amides themselves with this reagent has not been described. Alkaline hydrolysis of the basic reduction product gave in low yield 3-methylaminosalicylic acid, identical with an authentic sample, verifying the presence of the formanilide grouping in the antibiotic. While this

[1] Birch, Cameron, Harada, and Rickards, *Proc. Chem. Soc.*, 1960, 22.
[2] Dunshee, Leben, Keitt, and Strong, *J. Amer. Chem. Soc.*, 1949, **71**, 2436.
[3] Lockwood, Leben, and Keitt, *Phytopath.*, 1954, **44**, 438.
[4] Strong, "Topics in Microbial Chemistry," Squibb Lectures on Chemistry of Microbial Products, Wiley, New York, 1958, Vol. I, p. 1.
[5] Liu and Strong, *J. Amer. Chem. Soc.*, 1959, **81**, 4387.
[6] Watanabe, Tanaka, Fukuhara, Miyairi, Yonehara, and Umezawa, *J. Antibiotics, A*, 1957, **10**, 39.
[7] Yonehara and Takeuchi, *J. Antibiotics*, A, 1958, **11**, 254.
[8] Strong, Dickie, Loomans, van Tamelen, and Dewey, *J. Amer. Chem. Soc.*, 1960, **82**, 1513.
[9] Tener, Bumpus, Dunshee, and Strong, *J. Amer. Chem. Soc.*, 1953, **75**, 1100.
[10] van Tamelen, Strong, and Quarck, *J. Amer. Chem. Soc.*, 1959, **81**, 750.
[11] Tener, van Tamelen, and Strong, *J. Amer. Chem. Soc.*, 1953, **75**, 3623.
[12] Okumura, Masumura, and Horie, *J. Amer. Chem. Soc.*, 1959, **81**, 5215.
[13] Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publ. Inc., New York, 1956, p. 556.

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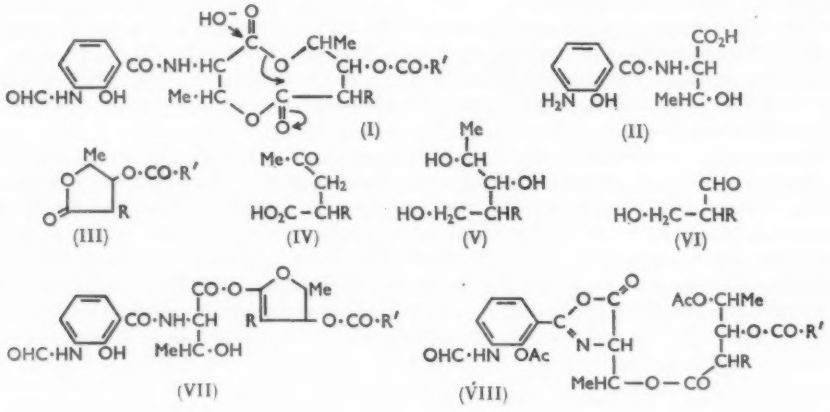
work was in progress, the isolation of blastmycic acid (*ar-N*-formylantimycic acid) from blastmycin [7] and also from antimycin-A [14] was reported, providing further confirmation.

3-Methylaminosalicylic acid was synthesised by methylation of 3-aminosalicylic acid with alkaline dimethyl sulphate, and isolated by chromatography as its methyl ester. No *O*-alkyl or dialkyl product was formed in this reaction, in accord with similar observations [15] on the methylation of 4-aminosalicylic acid. The required 3-aminosalicylic acid was prepared by a new route. In order to avoid the difficulty of separating the desired 3-nitro- from the more abundant 5-nitro-salicylic acid produced on nitration, salicylic acid was first brominated,[16] yielding almost entirely the 5-bromo-derivative. Nitration [17] then gave in good yield 5-bromo-3-nitrosalicylic acid, which was simultaneously reduced and debrominated with Raney alloy in alkali [18] to yield 3-aminosalicylic acid.

The neutral fragment formed on mild alkaline hydrolysis of antimycin-A showed infrared absorption (in CS_2) at 1788 and 1748 cm.$^{-1}$ compatible with the β-acyloxy-γ-lactone structure (as in III) proposed by van Tamelen, Strong, and Quarck [10] on the basis of reactions of model compounds and further alkaline hydrolysis to a mixture of acids whose major components were (+)-α-methylbutyric acid and an unidentified keto-acid, $C_{11}H_{20}O_3$. Blastmycinone, the corresponding degradation product of blastmycin which consists essentially of antimycin-A_3, was formulated by Yonehara and Takeuchi [7] as (III; R = n-C_4H_9, R′ = CH_2·$CHMe_2$) on degradative evidence, while, after completion of the present work, the neutral fragment from purified antimycin-A_1 was shown [14] to differ only in having R = n-C_6H_{13}. Vapour-phase chromatography of the neutral fragment resolved at least two components, confirming the earlier evidence of inhomogeneity [9] and indicating that the structural variations responsible for the different components of the antimycin-A complex resided in this portion of the molecule. Vigorous alkaline hydrolysis of the lactonic ester mixture (III) afforded a keto-acid fraction (IV), purified through the



semicarbazone and resolvable by paper chromatography of the ammonium salts [19] or vapour-phase chromatography of the methyl esters into two components present in comparable amounts, together with volatile acids identified by paper chromatography as branched-chain C_5 acids containing a trace of isobutyric acid.

[14] Liu, van Tamelen, and Strong, *J. Amer. Chem. Soc.*, 1960, **82**, 1652.
[15] Rosdahl, Swed. P. 133,598; *Chem. Abs.*, 1952, **46**, 10,204.
[16] Hewitt, Kenner, and Silk, *J.*, 1904, **85**, 1228.
[17] Lillman and Grothmann, *Ber.*, 1884, **17**, 2729.
[18] Cf. Schwenk, Papa, Whitman, and Ginsberg, *J. Org. Chem.*, 1944, **9**, 1.
[19] Reid and Lederer, *Biochem. J.*, 1951, **50**, 60.

Reduction, with lithium aluminium hydride, of antimycin-A or the neutral hydrolysis fragment gave the triol mixture (V), together with a volatile isopentyl alcohol fraction (discussed below). Oxidation of the triol mixture with unbuffered periodate yielded acetaldehyde as the only volatile aldehyde, and the aldol mixture (VI). While the aldol readily formed a 2,4-dinitrophenylhydrazone, its infrared spectrum ($\nu_{max.}$ in CS_2 3570, 3370, 1714 cm.$^{-1}$) showed only weak carbonyl absorption in accord with its expected existence [20] in the dimeric 1,3-dioxan form. Extended oxidation of the triol (V) with periodate in the presence of potassium hydrogen carbonate afforded in high yield a mixture of acids, shown by paper and vapour-phase chromatography to consist chiefly of n-valeric and n-heptanoic acid, together with small quantities of acetic and branched-chain C_5 acids arising from oxidation of residual acetaldehyde and isopentyl alcohols contaminating the triol.* While the oxidation of cyclic 1,3-diketones and aliphatic dicarbonyl compounds of the type R·CO·CHR'·COR", where R = OH or H, by periodate is well known,[21] no appreciable reaction has previously been observed with aldols.[22] These results confirm the β-acyloxy-γ-lactone structure (as in III) for the neutral fragment from hydrolysis of antimycin-A, and define the variation in alkyl substitution (R = n-C_4H_9, n-C_6H_{13}) present in antimycin-A (I) and its degradation products (III—VI).

Saponification of the lactone (III) from the antimycin-A complex had previously yielded (+)-α-methylbutyric acid, small discrepancies in physical properties of the acid being attributed to partial racemisation during hydrolysis.[9] Similar degradation of blastmycin afforded β-methylbutyric acid,[7] later isolated also from purified antimycin-A_1,[14] the major component of the antibiotic complex. In our hands the *p*-phenylphenacyl ester of the volatile acid obtained on saponification of the lactone (III) appeared to be a mixture. The volatile alcohol fraction, from lithium aluminium hydride reduction of antimycin (I) or the lactone (III) could not be resolved on vapour-phase chromatography but corresponded to isopentyl alcohol. The alcohols yielded an inhomogeneous 3,5-dinitrobenzoate, m. p. 53—61°, $[\alpha]_D$ +1·5°. White and Ratchford [23] report m. p. 83—84°, $[\alpha]_D$ +4·9° for the derivative of L-2-methylbutanol; the racemic derivative [24] had m. p. 70—70·5°; isopentyl 3,5-dinitrobenzoate had m. p. 63·7—64·5°. The volatile alcohol mixture is therefore either partially racemised *L*-2-methylbutanol or a mixture of this alcohol with 3-methylbutanol in the ratio 3 : 7 (calc. from optical rotations). We prefer the latter hypothesis since the infrared spectrum of the alcohols (R'·CH_2·OH) ($\nu_{max.}$ as liquid film 1388, 1373 cm.$^{-1}$) indicates the presence of a large proportion of *gem*-dimethyl component and is almost identical with that of commercial " isoamyl alcohol," $[\alpha]_D$ −1·0°. These results, together with the detection of a trace of isobutyric acid on hydrolysis (mentioned above), define the variation in the acyloxy-substituents (R' = CHMeEt, CH_2·$CHMe_2$, $CHMe_2$) in the lactone (III) and antimycin-A (I). Other natural products are known in which a similar mixture of side chains occurs.[25]

The various components of the antibiotic complex thus differ in the nature of the substituents R and R' in the hydrolysis product (III), and it remains to determine the mode of linkage in antimycin-A between (III) and the other primary cleavage product (II). The infrared spectrum of antimycin-A has absorption maxima (in CCl_4) at 3435 (NH), 1752 (ester), 1712 (*N*-formyl; cf. methyl 3-formamidosalicylate which has amide absorption at 1708 cm.$^{-1}$ in CS_2), 1646 (H-bonded aromatic amide), and 1518 cm.$^{-1}$ (amide), indicating

* Before we had completed work on this oxidation Dr. van Tamelen informed us that his independent work demonstrated the presence of an n-C_6H_{13} chain in antimycin-A_1.

[20] Owen, *Ann. Reports*, 1944, **41**, 139.
[21] Wolfrom and Bobbitt, *J. Amer. Chem. Soc.*, 1956, **78**, 2489.
[22] Cf. Bose, Foster, and Stephens, *J.*, 1959, 3314.
[23] White and Ratchford, *J. Amer. Chem. Soc.*, 1949, **71**, 1136; cf. Crombie and Harper, *J.*, 1950, 2685.
[24] Reichstein, *Helv. Chim. Acta*, 1926, **9**, 799.
[25] Birch, " Progress in the Chemistry of Organic Natural Products," Springer, Vienna, 1957, Vol. XIV, p. 200.

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the absence of a γ-lactone structure. The relative stability of the antibiotic in acidic conditions [4] renders unlikely the presence of ketal functions, or enolic linkages as have been proposed by American and Japanese workers in structures (as in VII) for antimycin-A [4] and blastmycin [7] respectively. Such formulæ were advanced to account for the lack of acidic functions other than a phenolic hydroxyl group, and for the extreme ease of formation of the γ-lactonic ester which is directly extractable from the alkaline hydrolysis medium without prior acidification. We propose the nine-membered dilactone ring structure (I; R = n-C_4H_9, n-C_6H_{13}; R′ = CHMeEt, CH_2·$CHMe_2$, $CHMe_2$). In the presence of base, transannular displacement occurs as indicated, assisted by compression in the medium ring [26] and juxtaposition of the appropriate oxygen and carbonyl functions. Similar nitrogen–carbonyl interaction has been observed,[27] and it is at a maximum in a nine-membered ring.

Japanese workers [7] treated blastmycin, now formulated as (I; R = n-C_4H_9, R′ = CH_2·$CHMe_2$), with acetic anhydride and pyridine to yield a compound $C_{30}H_{40}O_{11}N_2$, described on the basis of their structure (VII; R = n-C_4H_9; R′ = CH_2·$CHMe_2$) as *OO*-diacetylblastmycin although conclusive proof of the degree of acetylation was lacking. Since structure (I) does not admit an *OO*-diacetyl derivative, we examined the reaction of the antimycin-A complex with [*carbonyl*-^{14}C]acetic anhydride, finding that the product contained radioactivity corresponding to two acetyl residues. This radio-tracer approach enabled accurate acetyl determinations to be made in a case where conventional methods, such as saponification to volatile acids and *C*-methyl determination, were unreliable in view of the numerous interfering structures present. Mild alkaline hydrolysis of the diacetyl derivative afforded the lactonic ester (III) in high yield, excluding an oxazolone-type structure (VIII) which might result from rupture of the dilactone ring during acetylation (cf. the similar behaviour of some α-acylamino-esters [28]). The diacetyl compound showed infrared maxima (in CCl_4) at 3430 (NH), 1782 (phenolic OAc), 1752, 1734 (ester), 1714 (*N*-Ac) and 1677 cm.$^{-1}$ (aromatic amide), and ultraviolet absorption ($\lambda_{max.}$ 271 mμ; log ε 3·02) resembling that of benzamide [29] ($\lambda_{max.}$ 265; log ε 2·7); and on the basis of these spectra and reactions of model compounds this product is formulated as *ON*-diacetyldeformylantimycin-A, in which the *N*-formyl group of the antibiotic has been displaced by acetyl.

The lability of such *N*-formyl groups is well known. Nef [30] observed almost quantitative formation of acetanilide from formanilide and acetic anhydride, but his conditions were rather more vigorous than those used in the present work, where only unchanged formanilide was recovered. The presence of an *o*-hydroxyl group facilitates the displacement. *o*-Formamidophenol, a closer model for antimycin-A, yielded *o*-acetamidophenyl acetate together with a trace of *o*-acetamidophenol (resulting possibly from hydrolysis of the diacetyl compound during crystallisation from water); the *O*-methyl ether of antimycin-A is reported [8] unchanged on attempted acetylation. Replacement and migration of acyl substituents in *o*-aminophenols is extensive and complex.[31] In the case of antimycin-A the reaction does not appear to proceed through an *N*-acetyl-*N*-formyl stage which undergoes hydrolysis on crystallisation, since the same product is obtained under anhydrous conditions.

Experimental

Ultraviolet spectra were measured for EtOH solutions. Light petroleum refers to the fraction of b. p. 60—80°. Paper chromatograms were run on Whatman No. 1 paper. Radioactivity was assayed as described by Birch *et al.*[32]

[26] Cf. Prelog, in " Perspectives in Organic Chemistry," Interscience Publ. Inc., London, 1956, p. 96.
[27] Leonard, Fox, Oki, and Chiavarelli, *J. Amer. Chem. Soc.*, 1954, **76**, 630.
[28] Cornforth, in " Heterocyclic Compounds," ed. Elderfield, Wiley, New York, 1957, Vol. V, p. 340.
[29] Ley and Specker, *Ber.*, 1939, **72**, 199.
[30] Nef, *Annalen*, 1892, **270**, 278.
[31] Bell, *J.*, 1931, 2962.
[32] Birch, Massy-Westropp, Rickards, and Smith, *J.*, 1958, 360.

Antimycin-A.—The antibiotic complex, produced by a strain of *Streptomyces kitazawaensis*, had m. p. 143°, $\lambda_{max.}$ 229, 254 (infl.), 319 mμ (log ε 4·51, 4·02, 3·78), $\nu_{max.}$ (in CCl_4) 3435, 1752, 1712, 1646, 1518 cm.$^{-1}$.

Action of Alkali on Antimycin-A.—Hydrolysis [9] of antimycin-A (1·00 g.) with aqueous sodium hydroxide gave antimycic acid (170 mg.), m. p. 219—220° (decomp.) (from ethanol), $\nu_{max.}$ (in Nujol) 3348, 3220, 2590, 1659, 1628, 1599, 1578, 1539 cm.$^{-1}$, and the lactonic ester mixture (III) (450 mg.), a colourless oil, $\nu_{max.}$ (in CS_2) 1789, 1748 cm.$^{-1}$. Vapour-phase chromatography of the latter on a polyester column indicated the presence of at least two components.

Reduction of Antimycin-A by Lithium Aluminium Hydride.—Antimycin-A (1·0 g., 1·85 mmoles) in tetrahydrofuran (25 ml.) was added rapidly to a stirred, ice-cold suspension of lithium aluminium hydride (210 mg., 5·54 mmoles) in tetrahydrofuran (25 ml.). After 30 min. the mixture was brought to room temperature, kept there for 30 min., then refluxed briefly. The cooled mixture was acidified with 2N-hydrochloric acid and extracted with chloroform. The extracts, after being washed with aqueous potassium hydroxide, yielded a colourless oil (380 mg.) [still showing some carbonyl absorption ($\nu_{max.}$ in CCl_4 1769 cm.$^{-1}$)] which on further reduction by lithium aluminium hydride gave the triol (V).

The acidic aqueous liquors were neutralised, and the solution and precipitated inorganic solid were extracted separately with chloroform. The recovered oil (80 mg.), in saturated aqueous sodium hydroxide (3 ml.), was refluxed for 2 hr. under nitrogen. The solution was adjusted to pH 8—9 and washed with chloroform, then acidified (pH 3—4) and extracted with ether to yield 3-methylaminosalicylic acid (20 mg.), sublimed at 180°/10^{-2} mm., m. p. and mixed m. p. 209° (decomp.). Paper chromatography,[33] as the free acid, R_F 0·41 in methanol–pentyl alcohol–benzene–water (35 : 17·5 : 35 : 12·5), and as the ammonium salt, R_F 0·66 in methanol–pentyl alcohol–benzene–4% ammonia (35 : 17·5 : 35 : 12·5), confirmed the identity, spots being detected with ferric chloride or bisdiazotised benzidine reagents.

Brief treatment of the acid (13 mg.) with diazomethane in ether gave the ester (9 mg.) which, purified by chromatography on "Florisil" and crystallisation from light petroleum, had m. p. 54°, $\nu_{max.}$ (in CCl_4) 3474, 2820, 1678 cm.$^{-1}$, identical (mixed m. p. and infrared spectrum) with authentic methyl 3-methylaminosalicylate, m. p. 56—57·5°.

3-Aminosalicylic Acid.—To 5-bromo-3-nitrosalicylic acid [16,17] (280 mg.) in 5% aqueous sodium hydroxide (50 ml.) was added Raney alloy (2 g.) portionwise with stirring during 1·5 hr. After a further 30 min., the mixture was benzoylated under Schotten–Baumann conditions. The ether-extracted material obtained after acidification was steam-distilled to completion in the presence of 18N-sulphuric acid (5 ml.). The residual solution was filtered, extracted with ether, and adjusted to pH 3—4. Extraction with ethyl acetate afforded 3-aminosalicylic acid (70 mg.), m. p. 240° (decomp.) after sublimation at 180°/10^{-2} mm., identical {mixed m. p., R_F,[33] and infrared spectrum [(in Nujol) 2600, 1664sh, 1638, 1561 cm.$^{-1}$)]} with the product obtained by hydrogenating 3-nitrosalicylic acid in methanol in the presence of Adams catalyst.

Attempted extraction of the amino-acid from the acidified reduction mixture without benzoylation was unsuccessful.

Methyl 3-Methylaminosalicylate.—To 3-aminosalicylic acid (500 mg.) in 0·1N-aqueous sodium hydroxide (60 ml.), stirred at 80° under nitrogen, was added in 1·5 hr. dimethyl sulphate (900 mg.), with additional alkali as required. After acidification to pH 4, ether-extraction gave a solid (327 mg.), m. p. 223—236° after sublimation at 180°/10^{-2} mm. Paper chromatography [33] of this material showed the presence of 3-amino- and 3-methylamino-salicylic acids (R_F 0·25 and 0·41 respectively as the acids, 0·51 and 0·66 as the ammonium salts).

Crystallisation failed to resolve the mixture, which was treated with ethereal diazomethane; the bicarbonate-insoluble material (283 mg.) was chromatographed on "Florisil." Elution with pentane containing ether (1%) yielded *methyl 3-methylaminosalicylate* (54 mg.), m. p. 56—57·5° (from light petroleum). This gave a red-violet ferric test (Found: C, 59·3; H, 6·0. $C_9H_{11}NO_3$ requires C, 59·7; H, 6·1%). Elution with pentane–ether (4 : 1) gave methyl 3-aminosalicylate, long needles (from light petroleum), m. p. 87—88° (Tener *et al.*[11] record m. p. 85—85·5°), $\nu_{max.}$ (in CCl_4) 3502, 3418, 1681 cm.$^{-1}$.

3-Methylaminosalicylic Acid.—Methyl 3-methylaminosalicylate (5 mg.) in 10% aqueous sodium hydroxide (5 ml.) was refluxed for 2 hr. under nitrogen. The solution was extracted with ether at pH 8—9 and again at pH 4, the latter extract affording 3-methylaminosalicylic acid (4 mg.), m. p. 207° (decomp.) after sublimation at 180°/10^{-2} mm.

[33] Ekman, *Acta Chem. Scand.*, 1948, **2**, 383.

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Methyl 3-Formamidosalicylate.—3-Aminosalicylic acid (100 mg.) and 90% formic acid (1 ml.) were refluxed 10 min., diluted with water (3 ml.), and refrigerated. The filtered 3-formamidosalicylic acid had m. p. 215—220° (Zahn [34] records m. p. 215°). Brief treatment with ethereal diazomethane afforded *methyl 3-formamidosalicylate*, colourless needles, m. p. 126·5—127·5° (from light petroleum; charcoal), giving a violet ferric test (Found: C, 55·0; H, 4·4; N, 7·6. $C_9H_9NO_4$ requires C, 55·4; H, 4·6; N, 7·2%), $\nu_{max.}$ (in CS_2) 3408, 1708, 1676 cm.$^{-1}$. Paper chromatography [33] in methanol–pentyl alcohol–benzene–water (35 : 17·5 : 35 : 12·5) gave R_F 0·33.

Hydrolysis of the Lactonic Ester Mixture (III).—The ester mixture (III) (330 mg.) in 10% aqueous sodium hydroxide (5·5 ml.) was refluxed for 2 hr. Acidification and ether-extraction gave mixed acids (325 mg.). Paper chromatography as the ammonium salts [19] identified isobutyric (R_F 0·38, a trace) and a branched C_5 acid (0·53), while two further components (R_F 0·68, 0·78) were identical with the keto-acids (IV) obtained on hydrolysis of the semicarbazone mixture (see below). Vapour-phase chromatography on " polyester " and " silicone oil " columns of the acids as their methyl esters resolved three main components, identical in retention times with methyl isovalerate and the methyl esters of the keto-acids (IV).

Water (5 ml.) was added, the acid mixture distilled, and the distillate extracted with ether. The *p*-phenylphenacyl ester, m. p. 72·5—75·5° (from ethanol or light petroleum), obtained on treatment of the neutralised volatile acids with *p*-phenylphenacyl bromide in the usual way, could not be obtained homogeneous.

The aqueous, less volatile residue gave with semicarbazide a mixture (90 mg.), m. p. 132—138° (from ethanol), of the semicarbazones of the keto-acids (IV). Hydrolysis of this semicarbazone mixture (10 mg.) with warm N-hydrochloric acid (5 ml.) for 30 min. and ether-extraction afforded the keto-acids (IV), methylated with diazomethane to the keto-ester mixture, $\nu_{max.}$ (in CS_2) 1740, 1727 cm.$^{-1}$.

Reduction of the Lactonic Ester Mixture (III).—The lactonic ester mixture (III) (940 mg.) in ether (10 ml.) was added dropwise to lithium aluminium hydride (500 mg.) suspended in ether (10 ml.). After being kept overnight, the mixture was refluxed for 2 hr. The excess of reagent was destroyed, and the mixture acidified and extracted with ether. The clear oil (503 mg.) obtained on careful recovery was fractionated by short-path distillation; the short-chain alcohols were collected up to 130°/150 mm.; the triols (V) (333 mg.), $\nu_{max.}$ (in $CHCl_3$) 3560, 3385 cm.$^{-1}$, distilled at 130°/10^{-3} mm. as a colourless syrup.

The fraction of b. p. 130°/150 mm., $\nu_{max.}$ (liquid film) 3340, 1388, 1373 cm.$^{-1}$ {cf. commercial " isoamyl alcohol," $[\alpha]_D$ −1·0°, $\nu_{max.}$ (liquid film) 3332, 1387, 1371 cm.$^{-1}$} corresponded to isopentyl alcohol on vapour-phase chromatography and gave a 3,5-dinitrobenzoate mixture (275 mg.), plates, m. p. 50·5—56·5° after chromatography on " Florisil " and crystallisation from light petroleum, $[\alpha]_D^{22}$ +1·5° (6·7% in acetone) (Found: C, 51·4; H, 4·9; N, 10·1. Calc. for $C_{12}H_{14}N_2O_6$: C, 51·1; H, 5·0; N, 9·9%).

Periodate Oxidation of the Triol Mixture (V).—(i) To the triol mixture (V) (333 mg.) in dioxan (5 ml.) and water (5 ml.) was added aqueous 0·04N-sodium periodate (90 ml.), a nitrogen stream carrying volatile products into dinitrophenylhydrazine reagent. After 1 hr., utilisation of periodate corresponded to 0·95 oxygen atom per mole of triol. The precipitated 2,4-dinitrophenylhydrazone (30 mg.), after chromatography on alumina and crystallisation from methanol, had m. p. 162—164·5°, undepressed by acetaldehyde 2,4-dinitrophenylhydrazone, m. p. 164°. Comparison of infrared spectra and R_F values on paper chromatography in decalin–dimethylformamide [35] confirmed the identity.

Extraction of the aqueous oxidation solution with pentane afforded the aldol mixture (VI) (154 mg.), $\nu_{max.}$ (in CS_2) 3570, 3370, 1714 cm.$^{-1}$, with no significant ultraviolet absorption. The aldol (VI) (81 mg.) with Brady's reagent at room temperature gave a 2,4-dinitrophenylhydrazone which after filtration in ether through a short column of alumina (Peter Spence, Grade " H ") showed two spots on paper chromatography, one of R_F 0·10, the aldol derivative, the second, of R_F 0·83, probably a dehydration product thereof. After chromatography on alumina in ether, and crystallisation from ethyl acetate–light petroleum, the 2,4-dinitrophenylhydrazone of the aldol mixture (VI) was obtained as yellow crystals (82 mg.), m. p. 82·5—89·5°, $\nu_{max.}$ (in $CHCl_3$) 3595, 3452, 3322, 1623, and 1597 cm.$^{-1}$ (Found: C, 53·0; H, 6·4; N, 16·8. Calc. for $C_{15}H_{22}N_4O_5$: C, 53·2; H, 6·5; N, 16·6%.

[34] Zahn, *J. prakt. Chem.*, 1900, **61**, 532.
[35] Horner and Kirmse, *Annalen*, 1955, **597**, 48.

(ii) To the triol mixture (V) (30 mg.) in dioxan (2 ml.) was added aqueous 0·041N-sodium periodate (98 ml.). After utilisation of 1 mol. of periodate as in (i), no further uptake occurred during 20 hr. Further oxidation occurred on addition of sodium hydrogen carbonate (2 g.), and was complete 24 hr. later, when a total of 7 mol. of periodate had been utilised. Ether extracted neutral materials (4 mg.), then acidification and re-extraction gave a mixture of acids (19 mg.) in which acetic, n-valeric, and heptanoic acid were identified by paper chromatography,[18] as the ammonium salts (R_F 0·11, 0·56, and 0·70 respectively). Vapour-phase chromatography of the methylated acid mixture confirmed the presence of n-valeric and heptanoic acid, in addition to isovaleric acid.

ON-*Diacetyldeformylantimycin-A*.—Antimycin-A (50 mg.) was treated with acetic anhydride–pyridine (10 : 1; 1·8 ml.) at room temperature for 20 hr.,[7] yielding ON-*diacetyldeformylantimycin-A* (48 mg.), m. p. 134—138° (from aqueous ethanol) (Found: C, 60·5; H, 6·7; N, 5·0. $C_{29}H_{40}N_2O_{10}$ requires C, 60·4; H, 6·9; N, 4·9%). The derivative, $\nu_{max.}$ (in CCl_4) 3430, 1782, 1752, 1734, 1714, 1677 cm.$^{-1}$, $\lambda_{max.}$ 271 mμ (log ε 3·02), gave a negative ferric test.

Acetylation of antimycin-A and isolation of the product under anhydrous conditions by evaporation of the excess of reagents afforded the same diacetyl derivative (m. p. and infrared spectrum).

Acetylation of aniline with [*carbonyl*-^{14}C]acetic anhydride, prepared[36] from sodium [1-^{14}C]-acetate (15 μC) diluted to 13 g., gave acetanilide, m. p. 113—115° (Found: r.m.a. × 10^{-4}, 4·05). Acetylation of antimycin-A with this anhydride gave diacetyldeformylantimycin-A (Found: r.m.a. × 10^{-4}, 7·57. 2Ac require 8·10).

The diacetyl derivative (100 mg.) was shaken with 5% aqueous sodium hydroxide (1 ml.) for 10 min. Extraction with pentane gave the lactonic ester mixture (III) (35 mg., 79%), identified by infrared spectrum. Acidification and extraction with ether afforded a viscous intractable oil (43 mg.) giving a deep violet ferric test.

Acetylation of Model Compounds.—(i) Acetylation of 2-formamidophenol (62 mg.) with acetic anhydride–pyridine (10 : 1; 7 ml.) at room temperature for 20 hr., and dilution of the mixture with water, gave crystals (64 mg.), m. p. 114—125° (from water). Crystallisation from light petroleum gave the major, more soluble fraction as colourless needles, m. p. 122—123° after sublimation at 85°/0·1 mm., identified by mixed m. p. and infrared spectrum [$\nu_{max.}$ (in $CHCl_3$) 1772, 1694 cm.$^{-1}$] as *o*-acetamidophenyl acetate (prepared by similar acetylation of *o*-aminophenol). The less soluble fraction, m. p. 201—203°, gave a brown ferric test, and was identical (mixed m. p.) with *o*-acetamidophenol, m. p. 203·5° (from water), prepared by refluxing *o*-acetamidophenyl acetate (10 mg.) in 0·1N-aqueous potassium hydroxide (0·5 ml.) for 5 min.

(ii) Similar treatment of formanilide (100 mg.) with acetic anhydride–pyridine (9 ml.) yielded only starting material (45 mg.), m. p. and mixed m. p. 45—47°.

We are indebted to the Royal Commission for the Exhibition of 1851 for an Overseas Scholarship (D. W. C.), and thank Mrs. B. Moore for vapour-phase chromatograms.

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[36] Shantz and Rittenberg, *J. Amer. Chem. Soc.*, 1946, **68**, 210.

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188. *Some Complexes of Tertiary Phosphines with Ruthenium*(II) *and Osmium*(II).

By J. Chatt and R. G. Hayter.

The reactions of $RuCl_3$ and $(NH_4)_2OsCl_6$ with a variety of mono- and ditertiary phosphines are described. The properties, reactions, and structures of the resulting complexes, $[M_2Cl_3(PR_3)_6]Cl$ (M = Ru or Os; PR_3 = PMe_2Ph, PEt_2Ph, $PMePh_2$, or $PEtPh_2$), and *cis*- and *trans*-$[MX_2(chelate)_2]$ [chelate = $C_2H_4(PR_2)_2$ (R = Me, Et, or Ph), $CH_2(PPh_2)_2$, and *o*-$C_6H_4(PEt_2)_2$; X = halogen, SCN], are discussed.

In this laboratory we have recently prepared a number of planar organo- and hydrido-complexes of platinum and nickel having the metal–carbon and metal–hydrogen bonds stabilised by tertiary phosphines.[1] As a preliminary to the preparation of analogous octahedral complexes of ruthenium and osmium it was necessary to obtain octahedral complexes of tertiary phosphines with osmium and ruthenium halides. These were unknown, and in this paper we describe their preparation. The complexes of the chelating diphosphines proved most useful for our purpose and were most extensively studied; those of the monophosphines were investigated mainly as intermediates in the preparation of the chelate complexes.

It was expected that tertiary phosphines, with their tendency to form spin-paired complexes, would give octahedral complexes of Ru(II) and Os(II) in which the metals are in the stable d_ϵ^6 electronic state. Complexes of this type are known;[2] *e.g.*, $[MCl_2(AsMePh_2)_4]$, $[OsI_2(AsMePh_2)_3]_2$, $[MCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ (M = Ru or Os). We have found, in general, that ruthenium and osmium give similar complexes, minor differences being attributed to the greater relative size of osmium(II), to its greater susceptibility to oxidation, and to the lower rates of reaction of its complexes.

Complexes of Ditertiary Phosphines.—These were prepared as follows from the ditertiary phosphines, $C_2H_4(PR_2)_2$ (R = Me, Et, Ph), $CH_2(PPh_2)_2$, and *o*-$C_6H_4(PEt_2)_2$, and were all of the type $[MCl_2(\text{ditertiary phosphine})_2]$.

Method 1. *trans*-$[MCl_2(\text{ditertiary phosphine})_2]$. The *trans*-dichloro-complexes were prepared by refluxing a slight excess (*ca.* 10%) of the ditertiary phosphine with ruthenium trichloride or $(NH_4)_2OsCl_6$ in aqueous ethanol. All the ditertiary phosphines gave complexes of this type in reasonable yield (30—80%) as yellow or orange crystals. The *trans*-octahedral structures were confirmed by measurement of molecular weight (monomeric), conductivity (non-electrolytes), and dipole moment ($<1{\cdot}5$ D).

Method 2. *cis*-$[MCl_2(\text{ditertiary phosphine})_2]$. The *cis*-dichloro-isomers were prepared in high yields by reaction of the ditertiary phosphines with the monotertiary phosphine complexes [*e.g.*, I; X = Cl)] at 150—200° in the absence of solvent. Only $C_2H_4(PPh_2)_2$ in the ruthenium(II) series did not yield the *cis*-isomer in this manner, but a high yield of the *trans*-isomer was obtained instead. A model of *cis*-$[RuCl_2\{C_2H_4(PPh_2)_2\}_2]$ showed strain between the phenyl groups and this may be sufficient to cause isomerisation to the *trans*-form. However, the strain cannot be great because both *cis*-$[RuCl_2\{CH_2(PPh_2)_2\}_2]$, in which the steric requirements of the ligand are slightly less, and *cis*-$[OsCl_2\{C_2H_4(PPh_2)_2\}_2]$, in which the strain is relieved by a larger metal atom, have been prepared. In the preparation of the *cis*-osmium complex, the *trans*-isomer was also obtained in 60% yield.

The *cis*-octahedral structures were confirmed by measurement of molecular weight (monomeric in benzene), conductivity (non-electrolytes in nitrobenzene), and dipole

[1] Chatt and Shaw, *J.*, 1959, 705, 4020; 1960, 1718; Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343.

[2] Dwyer, Humpoletz, and Nyholm, *Proc. Roy. Soc., N.S.W.*, 1946, **80**, 217; Dwyer, Nyholm, and Tyson, *ibid.*, 1947, **81**, 272; Nyholm and Sutton, *J.*, 1958, 567, 572.

moment (8—11 D). The complexes *cis*-$[MCl_2\{C_2H_4(PR_2)_2\}_2]$ (R = Me, Et) and *cis*-$[RuCl_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$ also give conducting solutions in water, in which they are probably aquated, *e.g.*,

$$cis\text{-}[RuCl_2\{C_2H_4(PEt_2)_2\}_2] + H_2O \rightleftharpoons [RuCl(H_2O)\{C_2H_4(PEt_2)_2\}_2]^+ + Cl^-$$

Of the complexes prepared during the present study, only those of the type *cis*-$[OsX_2(chelate)_2]$ were appreciably oxidised in air. Oxidation was particularly noticeable when the chelate was $C_2H_4(PR_2)_2$ (R = Me or Et) and when the complexes were slightly impure; dark green or blue materials were formed.

Method 3. *cis*- and *trans*-$[MX_2(ditertiary\ phosphine)_2]$ (X = Br, I, SCN, CN, OAc). Complexes of this type were prepared from the corresponding *cis*- or *trans*-dichloro-complex by metathetical reaction with the appropriate metal salt (*e.g.*, LiBr) in solution. Most of the *trans*-complexes reacted only slowly in alcohol or tetrahydrofuran and some not at all. The products were best separated by chromatography (method 3*a*). The *cis*-complexes of ruthenium(II) were readily obtained in aqueous or aqueous-ethanolic solution. However, *cis*-$[OsCl_2\{C_2H_4(PEt_2)_2\}_2]$ was relatively slow to react with lithium iodide in acetone, about 16 hours' refluxing being required for complete reaction (method 3*b*). In neither case (3*a* or 3*b*) was any stereochemical inversion observed, and in both series reaction was slower with the bulkier ligands $[CH_2]_n(PPh_2)_2$ ($n = 1$ or 2). The great difference in reaction rates between the *trans*- and *cis*-isomers which is also observed in planar complexes, *e.g.*, *trans*- and *cis*-$[PtCl_2(PR_3)_2]$, may be attributed to the high *trans*-effect of the tertiary phosphine.

Method 4. *cis*-$[RuCl_2\{C_2H_4(PR_2)_2\}_2]$ (R = Me, Et). The complexes *trans*-$[RuCl_2\{C_2H_4(PR_2)_2\}_2]$ (R = Me or Et) react with an excess of aluminium trialkyls AlR'_3 (R′ = Me, Et, or Pr^n) at 60—80° in absence of solvent to give dark red oils of unknown composition. After the product has been washed with light petroleum, treatment with ethanol causes a vigorous reaction with gas evolution and formation of the corresponding *cis*-dichloro-complexes, identical with those obtained by method 2. *cis*- and *trans*-$[MCl_2\{(CH_2)_n(PPh_2)_2\}_2]$ ($n = 1$ or 2) give complex chloro-alkyls, on similar treatment,[3] while *trans*-$[OsCl_2\{C_2H_4(PR_2)_2\}_2]$ (R = Me or Et) do not yield crystalline products.

(I) $[(PhEt_2P)_3Ru{<}^{Cl}_{Cl}{>}Ru(PEt_2Ph)_3]^+X^-$

Complexes of Monotertiary Phosphines.—Mixed alkylarylphosphines react with aqueous-ethanolic ruthenium trichloride or ammonium hexachloro-osmate(IV) to give yellow or orange crystalline complexes, $[M_2Cl_3(PR_3)_6]Cl$ (PR_3 = PMe_2Ph, PEt_2Ph, $PMePh_2$, or $PEtPh_2$), to which we assign a symmetrical bridged structure of the type (I; X = Cl). The complexes are stable in air, can be recrystallised from alcohol or acetone, and are obtained even in the presence of a large excess of the tertiary phosphine, which might have been expected to split the bridge. The complex $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ is typical and was found to be almost completely dissociated into its constituent ions in boiling acetone, and to be a uni-univalent electrolyte in nitrobenzene and diamagnetic in the solid state. Derivatives could be prepared by replacement of the chloride anion and were found to be of the type [I; X = ClO_4, $O{\cdot}C_6H_2(NO_2)_3$, BPh_4, or SCN] consistent with the presence of a unique chloride ion in the parent complex. These observations are not consistent with the possible alternative structures $[Ru(PEt_2Ph)_6][RuCl_4]$ or $[Ru(PEt_2Ph)_4][RuCl_4(PEt_2Ph)_2]$. The three-membered chloro-bridge is suggested in order to retain octahedral ruthenium(II). The corresponding complexes of osmium(II) were assigned a structure similar to (I) on the basis of molecular-weight and conductivity measurements.

[3] Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153.

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The compound (I; X = SCN) is stable in the solid state but disproportionates in chloroform solution into (I; X = Cl) and an insoluble, possibly polymeric compound, which appears to contain both bridging and terminal thiocyanate groups, from the evidence of its infrared spectrum.[4]

Reactions of Monotertiary Phosphine Complexes.—The triple chloro-bridge in $[Ru_2Cl_3(PR_2Ph)_6]Cl$ (III; R = Me, Et) is not split by *p*-toluidine or hydrazine. Ditertiary phosphines, 1,1'-bipyridyl, and 1,10-phenanthroline slowly react with the complex (III; R = Et) in ethanol, displacing the monotertiary phosphine to give complexes of the type *cis*-$[RuCl_2(\text{ditertiary phosphine})_2]$, *cis*-$[RuCl_2(PEt_2Ph)_2(\text{bipy})]$ and *cis*-$[RuCl_2(PEt_2Ph)(1,10\text{-phen})]$ respectively.

The complexes $[Ru_2Cl_3(PRPh_2)_6]Cl$ (R = Me or Et) are less stable than those derived from PR_2Ph and react also with hydrazine, giving unstable red materials, probably of the type $[RuCl_2(PRPh_2)_2(N_2H_4)]$.

$[Os_2Cl_3(PR_3)_6]Cl$ reacts similarly with ditertiary phosphines to give *cis*-$[OsCl_2(\text{ditertiary phosphine})_2]$ and with cyclo-octa-1,5-diene to give $[OsCl_2(C_8H_{12})(PEtPh_2)_2]$.

Experimental

Microanalyses are by the Microanalytical Department of these Laboratories. M. p.s were determined on a Kofler hot-stage and are corrected. Alumina for chromatography was Spence's grade H, 100—200 mesh. The light petroleum had b. p. 60—80°. Molar conductivities were determined in nitrobenzene at 20°. The ruthenium trichloride and ammonium chloro-osmate were commercial products used without further purification.

The diphosphines $C_2H_4(PR_2)_2$ (R = Et or Ph) and $o\text{-}C_6H_4(PEt_2)_2$ were prepared as described by Chatt and Hart [5] and by Hart.[6] Bisdiphenylphosphinomethane was obtained by Dr. H. R. Watson by a method similar to that of Issleib and Müller,[7] and bisdimethylphosphinoethane as follows: [8]

All operations were carried out under nitrogen at *ca.* −70° with good stirring. Sodium (23·0 g.) was dissolved in liquid ammonia (*ca.* 500 c.c.), and dry phosphine (from zinc phosphide and hydrochloric acid) passed through the solution until the blue colour had been replaced by the yellow-green of monosodium phosphide $NaPH_2$. The colour was then just discharged by addition of methyl iodide (*ca.* 142 g.) in dry ether (50 c.c.) during ¾ hr. To the colourless solution was added a suspension of sodamide prepared from sodium (23 g.) in liquid ammonia (500 c.c.) to which had been added hydrated ferric nitrate (0·1—0·2 g.) as catalyst. The bright green colour of NaPHMe appeared and the solution was stirred for 1½ hr. to ensure completion of the reaction. The green colour was just discharged (to grey) by another addition of methyl iodide in ether, and dark red $NaPMe_2$ was formed by addition of sodamide as previously. 1,2-Dichloroethane (*ca.* 49·5 g.) in ether (40 c.c.) was then added slowly (20—25 min.), discharging the red colour through orange and green to dark grey. The final addition was made cautiously to avoid excess. The reactants were next allowed to warm to room temperature with slow stirring and complete evaporation of the ammonia (overnight). Boiled-out water was added at room temperature to dissolve the salts, and the diphosphine extracted with ether (500 c.c.) and worked up in the same way as one of the lower aliphatic monophosphines; this gave a 35—40% yield (26—30 g.) of a colourless liquid, b. p. 81—82°/26 mm. (Parshall [9] records 104°/60 mm.), characterised as its diquaternary *salt* $[Me_2P(C_2H_4)_2PMe_2]Br_2$ formed by reaction with ethylene dibromide in warm ethanol and recrystallised from aqueous ethanol (Found: C, 28·65; H, 6·0. $C_8H_{20}Br_2P_2$ requires C, 28·4; H, 6·0%).

o-Phenylenebisdimethylarsine was prepared as described by Chatt and Mann.[10]

Ditertiary Phosphine and Other Chelate Complexes.—*Method* 1, *trans*-$[MCl_2(\text{ditertiary phosphine})_2]$. trans-*Dichlorodi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*ruthenium*(II). Ruthenium trichloride (0·60 g., 2·88 mmoles) in water (15 ml.) was added to 1,2-bis(diethylphosphino)ethane

[4] Chatt, Duncanson, Hart, and Owston, *Nature*, 1958, **181**, 43, and references therein.
[5] Chatt and Hart, *J.*, 1960, 1378.
[6] Hart, *J.*, 1960, 3324.
[7] Issleib and Müller, *Chem. Ber.*, 1959, **92**, 3175.
[8] Cf. Wymore and Bailar, *J. Inorg. Nucl. Chem.*, 1960, **14**, 42.
[9] Parshall, *J. Inorg. Nucl. Chem.*, 1960, **14**, 291.
[10] Chatt and Mann, *J.*, 1939, 610.

(1·48 g., 7·20 mmoles) in ethanol (120 ml.) under nitrogen, and the solution refluxed for 2 hr. The black solution gradually became dark green and finally cleared to brown. Dilution with water (100 ml.) gave a yellow precipitate which, after crystallisation from aqueous ethanol, afforded the pure *complex* (0·64 g., 38%) as bright yellow rhombs, m. p. 241—242°, subliming at 200° [Found: C, 41·15; H, 8·3%; *M* (ebullioscopically in 0·5% benzene solution), 629. $C_{20}H_{48}Cl_2P_4Ru$ requires C, 41·1; H, 8·3%; *M*, 585]. This compound was a non-electrolyte and was also prepared in 83% yield by reaction between $[Ru(NH_3)_6]Cl_2$ and 1,2-bis(diethylphosphino)ethane at 200° in the absence of solvent or by a similar reaction between the ditertiary phosphine and *trans*-$[RuCl_2(AsMe_2Ph)_4]$. It was identified in both cases by mixed m. p.

The following complexes were similarly prepared.

trans-*Dichlorodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II), bright yellow prisms (55% yield) (from ethanol), m. p. 294°, subliming at 245° (Found: C, 30·4; H, 6·9. $C_{12}H_{32}Cl_2P_4Ru$ requires C, 30·5; H, 6·8%).

trans-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*ethane*]*ruthenium*(II), orange plates (from chloroform) (66% yield), which rapidly effloresced in air to a pale yellow powder, m. p. 284—285° (decomp.) (Found: C, 64·4; H, 5·2. $C_{52}H_{48}Cl_2P_4Ru$ requires C, 64·5; H, 5·0%); this compound was also obtained in almost quantitative yield by method 2 and in 25% yield by reaction between ruthenium trichloride and 1,2-bis(diphenylphosphino)ethane (2·5 mol.) at 230° for 24 hr.

trans-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*methane*]*ruthenium*(II), orange prisms (from chloroform), which lost solvent on drying in a vacuum at 80°, leaving a pale orange powder (75% yield), m. p. 276·5—278° (decomp.) (Found: C, 63·6; H, 4·9. $C_{50}H_{44}Cl_2P_4Ru$ requires C, 63·8; H, 4·7%). trans-*Dichlorodi*-[o-*phenylenebis*(*diethylphosphine*)]*ruthenium*(II), yellow needles (from ethyl acetate) (38% yield), m. p. 241—242° (decomp.) (Found: C, 49·2; H, 7·1. $C_{28}H_{48}Cl_2P_4Ru$ requires C, 49·4; H, 7·1%).

trans-*Di-iododi*-[1,2-*bis*(*diethylphosphine*)*ethane*]*ruthenium*(II) was prepared by a modification of method 1, the aqueous solution of ruthenium trichloride being treated with a 30-fold excess of aqueous sodium iodide, before addition of the diphosphine. After refluxing for 6½ hr., the brown precipitated product was filtered off and repeated crystallisation from benzene afforded the pure *complex* as orange-brown needles (8% yield), m. p. 267—270° (decomp.), subliming at 200° (Found: C, 31·6; H, 6·3; I, 33·9. $C_{20}H_{48}I_2P_4Ru$ requires C, 31·3; H, 6·3; I, 33·1%). A considerable quantity of a golden-yellow complex, probably containing mixed halides, was also obtained.

trans - *Dichlorodi*-[1,2 - *bis*(*diethylphosphino*)*ethane*]*osmium*(II). Bisdiethylphosphinoethane (2·86 g., 13·8 mmoles) in ethanol (200 ml.) and ammonium hexachloro-osmate(IV) (2·01 g., 4·6 mmoles) in water (200 ml.) were refluxed together for several hours, a clear red solution, probably containing Os(IV), being obtained. The reduction was completed by a few drops of hydrazine hydrate, and the resulting clear yellow solution was concentrated by distillation. Cooling gave yellow crystals, which afforded the pure *complex* from methanol as pale yellow irregular prisms (28%), m. p. 247—250° (decomp.) (Found: C, 35·75; H, 7·3. $C_{20}H_{48}Cl_2OsP_4$ requires C, 35·7; H, 7·2%).

trans-*Dichlorodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*osmium*(II) was similarly prepared and was purified by chromatography on alumina, being eluted as a purple band (yellow solution) by 1 : 9 ether–benzene. Crystallisation from methylcyclohexane afforded the pure complex as yellow prisms (30%), m. p. 298—300° (decomp.), subliming at 200° (Found: C, 26·0; H, 5·7. $C_{12}H_{32}Cl_2OsP_4$ requires C, 25·7; H, 5·75%). The following complexes were similarly prepared, except that the treatment with hydrazine hydrate was not necessary.

trans-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*ethane*]*osmium*(II), in 80% yield from chloroform, as large orange prisms, effloresing to yellow crystals, m. p. 293—296° (decomp.); this compound was identical with the major product obtained by reaction between $C_2H_4(PPh_2)_2$ and $[Os_2Cl_3(PEt_2Ph)_6]Cl$, and analysis indicates that it crystallises with ½$CHCl_3$ (Found: C, 57·4; H, 4·5; Cl, 8·8. $C_{52}H_{48}Cl_2OsP_4,\frac{1}{2}CHCl_3$ requires C, 57·3; H, 4·4; Cl, 9·7%). trans-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*methane*]*osmium*(II), from dimethylformamide solution by precipitation with methanol (70% yield), as golden-yellow needles, m. p. >350° (Found: C, 58·7; H, 4·5; Cl, 6·8. $C_{50}H_{44}Cl_2OsP_4$ requires C, 58·3; H, 4·3; Cl, 6·9%).

Method 2, *cis*-[MCl_2(ditertiary phosphine)$_2$]. cis-*Dichlorodi*-[1,2-*bis*(*diethylphosphino*)*ethane*]-*ruthenium*(II). Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (0·39 g., 0·29 mmole) and 1,2-bis(diethylphosphino)ethane (0·25 g., 1·20 mmoles) were heated together

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under nitrogen in the absence of solvent. At 145° reaction occurred with effervescence and the formation of a homogeneous pale yellow liquid. The temperature was raised to 200° to complete the reaction and, on cooling, the liquid partially solidified and was washed with light petroleum to remove the displaced diethylphenylphosphine. Crystallisation of the solid residue from ethyl acetate afforded the pure *complex* as lemon-yellow plates (0·25 g., 76%), m. p. 214—214·5° [Found: C, 40·9; H, 8·1%; *M* (ebullioscopically in benzene), 627 (0·45% solution); 610 (1·65%). $C_{26}H_{48}Cl_2P_4Ru$ requires C, 41·1; H, 8·3%; *M*, 585]. This compound is a non-electrolyte in nitrobenzene and has a molar conductivity in water of 92 ohm^{-1} ($8·57 \times 10^{-3}$M; 25°). The following complexes were similarly prepared.

cis-*Dichlorodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II), pale yellow prisms (from benzene) (85% yield), m. p. 263—264°, subliming at 230° [Found: C, 30·3; H, 6·8; Cl, 14·7%; *M* (ebullioscopically in methanol), 292 (0·68% solution), 289 (1·3%), 303 (2·2%). $C_{12}H_{32}Cl_2P_4Ru$ requires C, 30·5; H, 6·8; Cl, 15·0%; *M*, 1472]. This compound is a non-electrolyte in nitrobenzene, and has a molar conductivity in water of 142 ohm^{-1} ($5·34 \times 10^{-3}$M; 25°).

cis-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*methane*]*ruthenium*(II), canary-yellow rhombs (from chloroform) (80% yield), m. p. 273—273·5° (decomp.) (Found: C, 63·9; H, 4·7. $C_{50}H_{44}Cl_2P_4Ru$ requires C, 63·8; H, 4·7%).

cis-*Dichlorodi*-[o-*phenylenebis*(*diethylphosphine*)]*ruthenium*(II), yellow needles (from ethyl methyl ketone) (35% yield), m. p. 233—234·5° (decomp.) (Found: C, 49·4; H, 7·15. $C_{28}H_{48}Cl_2P_4Ru$ requires C, 49·4; H, 7·1%).

cis-*Dichlorodi*-[o-*phenylenebis*(*dimethylarsine*)]*ruthenium*(II), yellow prisms (from methanol) (87% yield), subliming above 300°, but not melting below 350° (Found: C, 32·4; H, 4·5. $C_{20}H_{32}As_4Cl_2Ru$ requires C, 32·3; H, 4·3%).

cis-*Dichlorobis*(*diethylphenylphosphine*)-1,1′-*bipyridylruthenium*(II), black needles (reddish-brown when crushed) (from benzene) (85% yield), m. p. >350° (Found: C, 54·8; H, 5·8; N, 4·3. $C_{30}H_{38}Cl_2N_2P_2Ru$ requires C, 54·5; H, 5·8; N, 4·2%). This compound is a non-electrolyte and does not react with 1,1′-bipyridyl (1 mole) at 230°.

cis-*Dichlorobis*(*diethylphenylphosphine*)-1,10-*phenanthrolineruthenium*(II), as black needles (dark red when crushed) (from ethanol) (85% yield), m. p. >350° (Found: C, 56·3; H, 5·8; N, 4·6. $C_{32}H_{38}Cl_2N_2P_2Ru$ requires C, 56·1; H, 5·6; N, 4·1%).

Similarly prepared from $[Os_2Cl_3(PEtPh_2)_6]Cl,2H_2O$ and chelate ligands were: cis-*dichlorodi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*osmium*(II), from methylcyclohexane in 80% yield as colourless needles, m. p. 208—211° (Found: C, 35·6; H, 7·1. $C_{20}H_{48}Cl_2OsP_4$ requires C, 35·7; H, 7·2%). cis-*Dichlorodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*osmium*(II), in 65% yield by sublimation at 260° *in vacuo* as colourless crystals, m. p. 295—305° (decomp.) (Found: C, 26·0; H, 5·75. $C_{12}H_{32}Cl_2OsP_4$ requires C, 25·7; H, 5·7%).

cis-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*ethane*]*osmium*(II) was obtained in 40% yield by reaction between $C_2H_4(PPh_2)_2$ and $[Os_2Cl_3(PEt_2Ph)_6]Cl$: extraction of the crude product with tetrahydrofuran gave a pink solution and evaporation and crystallisation from ethyl acetate afforded the pure *complex* as pale yellow prisms, m. p. 290—291° (decomp.) (Found: C, 59·0; H, 5·0. $C_{52}H_{48}Cl_2OsP_4$ requires C, 59·0; H, 4·6%). The tetrahydrofuran-insoluble portion of the crude product (60% of total) consisted mainly of *trans*-$[OsCl_2\{C_2H_4(PPh_2)_2\}_2]$, which was obtained from chloroform in the solvated form (Found: C, 57·3, 56·9; H, 4·55, 4·4%). Crystallisation from dimethylformamide–methanol gave the unsolvated complex as pale yellow plates, m. p. 295—297° (decomp.) (Found: C, 59·4; H, 4·7; Cl, 6·6. $C_{52}H_{48}Cl_2OsP_4$ requires C, 59·0; H, 4·6; Cl, 6·7%).

cis-*Dichlorodi*-[1,2-*bis*(*diphenylphosphino*)*methane*]*osmium*(II), pale yellow feathery needles (from nitrobenzene–methanol) (85% yield), m. p. >350° (Found: C, 58·2; H, 4·45. $C_{50}H_{44}Cl_2OsP_4$ requires C, 58·3; H, 4·3%). This compound is solvated on crystallisation from chloroform (Found: C, 52·8; H, 4·1. $C_{50}H_{44}Cl_2OsP_4,CHCl_3$ requires C, 53·3; H, 3·95%); the solvent was only partially removed after 10 hr. *in vacuo* at 80° (Found: C, 53·8; H, 4·2%).

cis-*Dichlorodi*-[o-*phenylenebis*(*diethylphosphine*)]*osmium*(II), solvated pale yellow rhombs (80% yield) (from benzene), m. p. 258—270° (decomp.) (Found: C, 48·3; H, 6·4. $C_{28}H_{48}Cl_2OsP_4,C_6H_6$ requires C, 48·2; H, 6·4%).

Dichlorocyclo-octa-1,5-*dienedi*(*ethyldiphenylphosphine*)*osmium*(II), khaki-coloured (30% yield) (from light petroleum), m. p. 135—142° (decomp.) (Found: C, 54·1; H, 5·3. $C_{36}H_{42}Cl_2OsP_2$ requires C, 54·2; H, 5·3%).

Method 3. (a) trans-*Isomers*, *trans*-[MX_2(ditertiary phosphine)$_2$] (X = Br, I, CN, OAc). trans-*Dibromodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II). *trans*-Dichlorodi-[1,2-bis-(dimethylphosphino)ethane]ruthenium(II) (0·50 g.) was refluxed in ethanol with lithium bromide (4·6 g., 30-fold excess) for 2 days, the solution slowly changing in colour from yellow to orange. The solvent was removed at 12 mm., and the water-insoluble residue dissolved in benzene (10 ml.) and chromatographed on alumina. Elution with benzene containing 20% of light petroleum gave the pure *complex*, which crystallised from acetone as orange prisms (37%), m. p. 286·5—289° (decomp.), subliming at 200° (Found: C, 25·4; H, 5·8. $C_{12}H_{32}Br_2P_4Ru$ requires C, 25·7; H, 5·75%). Elution with methanol gave unchanged dichloro-complex (0·26 g.).

The following complexes were similarly prepared.

trans-*Di-iododi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II) was eluted with benzene and crystallised from ethyl methyl ketone as brick-red prisms (35% yield), m. p. 302·5—304° (decomp.), subliming at 250° (Found: C, 22·1; H, 4·9. $C_{12}H_{32}I_2P_4Ru$ requires C, 22·0; H, 4·9%).

trans-*Dibromodi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*ruthenium*(II) was eluted with benzene containing 20% of light petroleum and crystallised from 50% benzene–light petroleum as pale orange needles (25% yield), m. p. 264·5—266° subliming at 220° (Found: C, 35·9; H, 7·2. $C_{20}H_{48}Br_2P_4Ru$ requires C, 35·7; H, 7·2%).

trans-*Dicyanodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II) *monohydrate* was eluted with 1 : 19 methanol–benzene and crystallised from acetone as colourless needles (48% yield), m. p. >350°, subliming at 300° (Found: C, 35·6; H, 7·5; N, 6·2. $C_{14}H_{34}N_2OP_4Ru$ requires C, 35·7; H, 7·3; N, 5·9%). Water of hydration was not removed after heating in a vacuum at 100° for 16 hr. The infrared spectrum (Nujol mull) showed a strong band at 2064 cm.$^{-1}$ attributed to $\nu_{C\equiv N}$.

trans-*Diacetatodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II) *monohydrate* was obtained from acetone as colourless prisms (70% yield), m. p. 245—260° (decomp.), subliming at 180° (Found: C, 35·7; H, 7·6. $C_{16}H_{38}O_5P_4Ru,H_2O$ requires C, 35·75; H, 7·5%); this compound decomposed on attempted chromatography; its infrared spectrum (hexachlorobutadiene mull) shows two strong doublet bands at 1603, 1570, and 1433, 1395 cm.$^{-1}$, both due to the unidentate acetate groups.

trans-*Di-iododi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*osmium*(II), from dimethylformamide in 55% yield as light orange needles, m. p. 272—274° (decomp.), subliming at 220° (Found: C, 28·5; H, 5·8. $C_{20}H_{48}I_2OsP_4$ requires C, 28·05; H, 5·65%).

(b) cis-*Isomers*, cis-[MX_2(ditertiary phosphine)$_2$] (X = Br, I, SCN). cis-*Dibromodi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*ruthenium*(II). *cis*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]-ruthenium(II) (0·50 g.) was dissolved in hot water (40 ml.), and the solution was filtered, and added to a solution of potassium bromide (1·0 g.) in water (3 ml.). The yellow precipitate was filtered off and washed with water; crystallisation from ethanol afforded the pure *complex* as yellow plates (88% yield), m. p. 191° (Found: C, 35·9; H, 7·2. $C_{20}H_{48}Br_2P_4Ru$ requires C, 35·7; H, 7·2%).

The following complexes were similarly prepared.

cis-*Di-iododi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*ruthenium*(II), obtained from chloroform as orange-brown prisms (90% yield), had m. p. 263—264° (decomp.), subliming at 260° (Found: C, 31·4; H, 6·3; I, 32·6. $C_{20}H_{48}I_2P_4Ru$ requires C, 31·3; H, 6·3; I, 33·1%).

cis-*Dithiocyanatodi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*ruthenium*(II) formed, from aqueous acetone, colourless prisms (74% yield), m. p. 325—326·5° (decomp.), subliming at 300° (Found: C, 41·75; H, 7·55; N, 4·6. $C_{22}H_{48}N_2P_4RuS_2$ requires C, 42·0; H, 7·7; N, 4·45%); the infrared spectrum (Nujol mull) shows a strong doublet band at 2110, 2105 cm.$^{-1}$ due to $\nu_{C\equiv N}$.

cis-*Dibromodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II), yellow prisms (from ethanol) (50% yield), m. p. 242—243° (decomp.) (Found: C, 26·05; H, 5·7. $C_{12}H_{32}Br_2P_4Ru$ requires C, 25·7; H, 5·75%).

cis-*Di-iododi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II), golden-yellow prisms (from ethanol) (55% yield), m. p. 289—291° (decomp.) (Found: C, 22·2; H, 4·9; I, 38·3. $C_{12}H_{32}I_2P_4Ru$ requires C, 22·0; H, 4·9; I, 38·7%).

cis-*Dithiocyanatodi*-[1,2-*bis*(*dimethylphosphino*)*ethane*]*ruthenium*(II), colourless plates (from acetone) (75% yield), decomp. 328° (Found: C, 32·9; H, 6·5; N, 5·1. $C_{14}H_{32}N_2P_4RuS_2$

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requires C, 32·5; H, 6·2; N, 5·4%); the infrared spectrum (Nujol mull) has a strong doublet band at 2108, 2102 cm.$^{-1}$ due to $\nu_{C\equiv N}$.

cis-*Di-iododi*-[o-*phenylenebis*(*diethylphosphine*)]*ruthenium*(II), golden-yellow prisms (from ethyl methyl ketone) (65% yield), m. p. 247—248° (decomp.) (Found: C, 40·1; H, 5·8. $C_{28}H_{48}I_2P_4Ru,\frac{1}{2}C_4H_8O$ requires C, 40·1; H, 5·8%); the solvent of crystallisation was not removed after 6 hr. in a vacuum at 100°.

cis-*Di-iododi*-[1,2-*bis*(*diethylphosphino*)*ethane*]*osmium*(II). *cis*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]osmium(II) (0·25 g.) and lithium iodide (1·0 g.) were dissolved in acetone and heated under reflux for 16 hr. to give a white precipitate and a pale yellow solution. Solvent was removed at 15 mm., and the water-insoluble residue crystallised from ethanol in a nitrogen atmosphere to give the pure *complex* (80% yield) as pale yellow needles, m. p. 221·5—222·5° (slight decomp.); recrystallisation occurs above 225° and the m. p. is then 260—266° (decomp.) (Found: C, 28·3; H, 5·8. $C_{20}H_{48}I_2OsP_4$ requires C, 28·05; H, 5·65%).

Method 4, *cis*-$[RuCl_2\{C_2H_4(PR_2)_2\}_2]$ (R = Me, Et). cis-*Dichlorodi*-[1,2-*bis*(*diethylphosphino*)-*ethane*]*ruthenium*(II). *trans*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II) (0·20 g.) was warmed with triethylaluminium (0·25 ml.) under nitrogen at 60—80° to give a dark red oil. After about 5 min., the oil was well washed with light petroleum to remove excess of triethylaluminium; it was then suspended in light petroleum, and ethanol was added dropwise. A vigorous reaction with effervescence occurred and the oil dissolved to give a pale yellow solution, which deposited crystals on cooling; these were filtered off and crystallisation from benzene containing 50% of light petroleum afford the pure cis-*isomer* (0·15 g., 75%), m. p. 210—213° (Found: C, 40·9; H, 8·2. $C_{20}H_{48}Cl_2P_4Ru$ requires C, 41·1; H, 8·3%). The dimethylphosphino-analogue was similarly prepared in 50% yield.

Monotertiary Phosphine Complexes.—Tri-μ-chlorohexakis(*diethylphenylphosphine*)*diruthenium*(II) *chloride*. Ruthenium trichloride (12·9 g., 0·062 mole) in water (400 ml.) and diethylphenylphosphine (46·1 g., 0·28 mole) in methanol (1200 ml.) were refluxed together under nitrogen for 24 hr., the colour of the solution changing from black through dark green to clear orange-yellow. When the yellow colour was obtained, the solution was concentrated to about half its original volume and, on cooling, deposited yellow crystals. This product was filtered off and, after being washed with methanol, was sufficiently pure for use as raw material for the preparation of the ditertiary phosphine complexes (yield 32·2 g., 75%). The pure *complex* was obtained from methanol as canary-yellow needles, m. p. 150—152° [Found: C, 53·4; H, 6·9%; *M* (ebullioscopically in acetone), 822 (0·23% solution), 753 (3·25%). $C_{60}H_{90}Cl_4P_6Ru_2$ requires C, 53·7; H, 6·8%; *M*, 1341]. This compound is diamagnetic in the solid state and has a molar conductivity in nitrobenzene of 23·5 ohm^{-1} ($4·6 \times 10^{-3}$M) and in acetone of 116 ohm^{-1} ($2·66 \times 10^{-3}$M).

The following complexes were similarly prepared.

Tri-μ-chlorohexakis(*dimethylphenylphosphine*)*diruthenium*(II) *chloride dihydrate* separated in 80% yield from methanol as bright yellow crystals, m. p. 118—120° [Found: C, 47·7; H, 5·7%; *M* (ebullioscopically in acetone), 464 (1·04% solution), 484 (1·52%). $C_{48}H_{66}Cl_4P_6Ru_2,2H_2O$ requires C, 47·7; H, 5·8%; *M*, 1209]. Molar conductivity 26·2 ohm^{-1} ($2·04 \times 10^{-3}$M).

Tri-μ-chlorohexakis(*ethyldiphenylphosphine*)*diruthenium*(II) *chloride trihydrate* was obtained from methanol as orange crystals (55% yield), m. p. 134·5—135° (decomp.) [Found: C, 59·9; H, 5·7%; *M* (ebullioscopically in acetone), 645 (1·41% solution), 710 (2·21%). $C_{84}H_{90}Cl_4P_6Ru_2,3H_2O$ requires C, 59·9; H, 5·75%; *M*, 1683·5]. Molar conductivity 17·5 ohm^{-1} ($1·72 \times 10^{-3}$M).

Tri-μ-chlorohexakis(*methyldiphenylphosphine*)*diruthenium*(II) *chloride trihydrate* separated from ethanol (65% yield) as orange crystals, m. p. 175—178° (decomp.) (Found: C, 58·75; H, 5·4. $C_{78}H_{78}Cl_4P_6Ru_2,3H_2O$ requires C, 58·6; H, 5·3%). Molar conductivity 21·2 ohm^{-1} ($2·82 \times 10^{-3}$M).

Tri-μ-chlorohexakis(*diethylphenylphosphine*)*diruthenium*(II) *picrate* was precipitated on treating an ethanolic solution of (I; X = Cl) with aqueous sodium picrate. The complex was filtered off, washed with water, and crystallised twice from aqueous acetone, forming lemon-yellow plates, m. p. 153·5—155° (decomp.) (Found: C, 51·9; H, 6·3; N, 2·8. $C_{66}H_{92}Cl_2N_3O_7P_6Ru_2$ requires C, 51·7; H, 6·0; N, 2·75%). Molar conductivity 19·3 ohm^{-1} ($1·93 \times 10^{-3}$M). *Tri-μ-chlorohexakis*(*diethylphenylphosphine*)*diruthenium*(II) *perchlorate monohydrate* was precipitated by treating an ethanolic solution of (I; X = Cl) with an excess of

20% perchloric acid; recrystallisation from ethanol afforded the pure complex as yellow needles (70% yield), m. p. 149·5—151° (decomp.) (Found: C, 50·6; H, 6·3. $C_{80}H_{90}Cl_4O_4Ru_2,H_2O$ requires C, 50·6; H, 6·5%). Molar conductivity 24·6 ohm^{-1} (1·9 × 10^{-3}M).

Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) *tetraphenylborate* was precipitated on treating an ethanolic solution of (I; X = Cl) in ethanol with 100% excess of ethanolic sodium tetraphenylborate. The precipitate was filtered off and washed with water and ethanol; three crystallisations from acetone afforded the pure complex as yellow microcrystals,

Dipole moments.

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^3\Delta n/\omega$	$-\Delta v/\omega$	$_TP$	$_EP$	$_OP$	μ (D)
trans-[$RuCl_2\{C_2H_4(PEt_2)_2\}_2$]							
3·726	0·521						
4·671	0·565						
7·822	0·539		(0·53)	167 *	(133)	14 *	*0·85* *
cis-[$RuCl_2\{C_2H_4(PEt_2)_2\}_2$]							
3·090	18·186						
3·621	17·978						
4·067	17·985						
12·33		7·90					
20·32		9·09					
4·545			0·572				
5·277			0·493	2097	132·9	1944	*9·75*
cis-[$RuI_2\{C_2H_4(PEt_2)_2\}_2$]							
1·873	15·581						
4·224	15·591						
7·457		8·24					
9·600		8·04					
9·126			0·559	2388	167	2196	*10·35*
trans-[$RuCl_2\{C_2H_4(PMe_2)_2\}_2$]							
4·627	0·536						
7·223	0·543						
6·492			0·493				
19·82		7·94					
25·57		8·37		140	112	11	*0·75*
trans-[$RuCl_2\{o\text{-}C_6H_4(PEt_2)_2\}_2$]							
6·282	0·723		(0·35)	217 *	(181)	9·6 *	*0·7*
cis-[$RuCl_2\{CH_2(PPh_2)_2\}_2$]							
3·655	11·47						
5·220	10·88		(0·53)	2154 *	(266)	1848 *	*9·5* *
cis-[$RuCl_2(PEt_2Ph)_2$(1,1′-bipyridyl)]							
0·982	20·52						
0·9975	20·77		(0·53)	2691 *	(177)	2487 *	*11·0* *
cis-[$OsCl_2\{C_2H_4(PEt_2)_2\}_2$]							
1·186	14·44						
2·398	14·24						
34·17		7·71					
44·62		8·06					
4·296			0·535	1942	150	1770	*9·3*
cis-[$OsCl_2\{C_2H_4(PPh_2)_2\}_2$]							
1·319	7·649						
1·441	7·638		(0·53)	1716 *	(269)	1407 *	*8·3* *

Estimated values are in parentheses. * Calc. by using estimated values of densities and refractivities.

m. p. 156—159° (decomp.) (Found: C, 1·9; H, 7·15. $C_{84}H_{110}BCl_3P_6Ru_2$ requires C, 62·1; H, 6·8%).

Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) *thiocyanate* was precipitated as pale yellow plates (m. p. 160—161°) by mixing cold filtered solutions of (I; X = Cl) in ethanol and potassium thiocyanate (10-fold excess) in water. The complex was filtered off, washed successively with water and ethanol, and dried *in vacuo* (Found: C, 53·45; H, 6·6; N, 1·2.

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$C_{61}H_{90}Cl_3NP_6Ru_2S$ requires C, 53·7; H, 6·65; N, 1·0%). Molar conductivity 27·7 ohm^{-1} (2·04 × 10^{-3}M-solution). The infrared spectrum (Nujol mull) shows a strong band at 2053 cm.$^{-1}$ attributed to $\nu_{C\equiv N}$ of the thiocyanate anion. This complex was insoluble in most organic solvents but, in chloroform, it rapidly disproportionated into $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ (identified by mixed m. p. with an authentic specimen) and an insoluble, unidentified, pale yellow compound (m. p. >350°, blackening at 260°) (Found: C, 51·9; H, 6·3; N, 3·1%). Molar conductivity 3·6 ohm^{-1} (6·9 × 10^{-4}M, for $M \approx 1450$). Its infrared spectrum (Nujol mull) contains bands at 2117 cm.$^{-1}$ (strong) and at 2145 cm.$^{-1}$ (medium) attributed to terminal and bridging $\nu_{C\equiv N}$ respectively.

Tri-μ-chlorohexakis(ethyldiphenylphosphine)diosmium(II) *chloride dihydrate.* Ethyldiphenylphosphine (7·53 g., 35·0 mmoles) in ethanol (400 ml.) was refluxed with ammonium hexachloroosmate(IV) (3·84 g., 8·75 mmoles) in water (100 ml.) for 6 hr. A dark red precipitate was first obtained, which slowly dissolved to give a greenish-yellow colour and finally a clear orange-yellow solution. Cooling gave yellow crystals (7·51 g., 95%) of crude product, which was obtained pure from ethanol as yellow-orange plates, m. p. 180—182° (decomp.) [Found: C, 54·7; H, 5·2%; *M* (ebullioscopically in acetone), 980 (1·07% solution), 955 (1·80%). $C_{84}H_{94}Cl_4O_2Os_2P_6$ requires C, 54·7; H, 5·1%; *M*, 1844]. Molar conductivity 21·6 ohm^{-1} (2·8 × 10^{-3}M).

The following compounds were similarly prepared.

Tri-μ-chlorohexakis(methyldiphenylphosphine)diosmium(II) *chloride* separated in 40% yield from ethanol as bright yellow crystals, m. p. 185—186° (decomp.) (Found: C, 54·2; H, 4·7. $C_{78}H_{78}Cl_2Os_2P_6$ requires C, 54·4; H, 4·6%). Molar conductivity 24·4 ohm^{-1} (2·0 × 10^{-3}M). *Tri-μ-chlorohexakis(diethylphenylphosphine)diosmium*(II) *chloride* was isolated in 85% yield from methanol as lemon-yellow needles, m. p. 178·5—180° (decomp.) (Found: C, 47·3; H, 5·9. $C_{60}H_{90}Cl_4Os_2P_6$ requires C, 47·4; H, 6·0%). Molar conductivity 20·4 ohm^{-1} (3·8 × 10^{-3}M).

Ditertiary Phosphine Complexes of Ruthenium(III).—trans-*Dichlorodi-*[1,2-*bis(diethylphosphino)ethane]ruthenium*(III) *perchlorate.* *trans*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]-ruthenium(II) (0·10 g.) in ethanol (5 ml.) was treated with 20% perchloric acid (2 ml.) to give, on warming, a clear dark green solution. On cooling, dark green crystals separated, which, after crystallisation from ethanol containing a little perchloric acid, afforded the pure *complex* as dark green needles (60%), m. p. 172—173·5° (decomp.) (Found: C, 35·0; H, 7·1; Cl, 15·7. $C_{20}H_{48}Cl_3O_4P_4Ru$ requires C, 35·1; H, 7·1; Cl, 15·55%). cis-*Dichlorodi-*[1,2-*bis(diethylphosphino)ethane]ruthenium*(III) *perchlorate* was similarly prepared in 70% yield from the *cis*-dichloro-isomer as dark green needles, m. p. 167·5—169·5° (decomp.) (Found: C, 34·9; H, 7·1; Cl, 15·7%).

Dipole Moments.—These (see Table) were determined as described in ref. 1, where the meanings of the symbols are also given.

The authors thank Dr. F. A. Hart for a gift of *o*-phenylenebis(diethylphosphine) and Dr. H. R. Watson for the first samples of $[CH_2]_n(PPh_2)_2$ (n = 1 and 2).

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[*Received, August* 31*st*, 1960.]

189. *Electron-transfer Reactions between Oxygen and Aromatic Hydrocarbons.*

By W. Ij Aalbersberg, J. Gaaf, and E. L. Mackor.

The reversible formation of the perylene monopositive ion from perylene and molecular oxygen in solutions of varying acidity in the presence of oxygen up to 100 atm. has been investigated. The monopositive ion is not formed in acetic acid, but is readily formed in trifluoroacetic acid in contact with air.

The equilibrium was studied in mixtures of trifluoroacetic and acetic acid. It appears that the oxygen molecule takes up one electron and that an ion pair $M^+ \cdot O_2^-$ (M = perylene) is formed. It is estimated that the average life-time of the complex in $CF_3 \cdot CO_2H$ is about 10^{-7} sec.

The change of line shape and the loss of hyperfine structure of the electron-spin resonance spectrum of the perylene positive ion in solutions of different acidity and viscosity, and the influence of oxygen, were investigated. The broadening of the spectrum in $CF_3 \cdot CO_2H$ is in agreement with an electron transfer with a frequency of about 10^7 sec.$^{-1}$.

In a previous paper [1] it was reported that the proton complexes of strongly basic aromatic hydrocarbons can be transformed into their monopositive ions when brought into contact with molecular oxygen. The reaction appeared to be reversible. However, the nature of the compounds formed from oxygen remained unexplained.

The effect of the oxygen pressure on the equilibrium between the perylene molecule and its monopositive ion in a weak acid has now been studied.[2]

Experimental

The apparatus for handling solutions in hydrogen fluoride as well as the high-pressure absorption cell have been described elsewhere.[2] A Cary model 11 spectrometer was used for recording the ultraviolet spectra.

The electron-spin resonance (E.S.R.) spectra were measured with a Varian V 4500 spectrometer, which operates at a nominal frequency of 9400 Mc./sec. A 6-inch magnet was used. The magnetic field, which was modulated with a frequency of 100 kc./sec., was determined with a precision gaussmeter model M 2 of Nuclear Magnetics Corporation.

The electron-spin resonance spectrum of perylene in hydrogen fluoride has been measured by using a probe made of Teflon of 0·8 mm. internal and 5 mm. external diameter. Even with this small internal diameter the high dielectric loss of hydrogen fluoride caused a significant decrease in the quality factor of the cavity.

The spectra at low temperature were measured by insertion of a vacuum-jacketed Dewar glass tube in the cavity; the quality of the cavity decreased considerably and relatively poor spectra were obtained.

The chemicals were of the same source as previously.[1] Nitric oxide (Matheson Inc.) was used without further purification.

Results

The experiments with various hydrocarbons M in strong acids indicated that in the presence of oxygen an equilibrium exists between proton complex MH^+ and monopositive ion M^+.[1] * In this reaction an electron is transferred from the hydrocarbon to the oxygen molecule, but whether oxygen takes up one or two electrons remained uncertain.

* Nitric oxide in acidic solutions can also act as an electron-acceptor. At small pressures ($\ll$1 atm.) it converts the proton complexes of 3,4-benzopyrene and pyrene in hydrogen fluoride into their monopositive ions. At higher pressures (2 atm.) 1,2-benzanthracene is almost completely converted into its positive ion, which indicates that nitric oxide is a better acceptor than oxygen in hydrogen fluoride. The reactions with nitric oxide were not further investigated.

[1] Aalbersberg, Hoijtink, Mackor, and Weijland, *J.*, 1959, 3049.
[2] Cf. Aalbersberg, Thesis, Free University, Amsterdam, 1960.

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An attempt to establish the reaction equation by spectroscopic determination of the ratio $[M^+]/[MH^+]$ failed because the conversion of the proton complexes of perylene and tetracene into their monopositive ions is nearly quantitative even at low oxygen pressures, whereas the proton complexes of other hydrocarbons studied decompose or form precipitates at higher oxygen pressures.

Absorption Spectra.—Fig. 1 shows that the stability of the positive ion decreases at lower acidity of the solvent. In $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (29 mole % of complex; $H_0 = -9{\cdot}22$; cf. ref. 1) perylene is converted nearly quantitatively into the monopositive ion on contact with air (Fig. 1a), whereas a solution of perylene in acetic acid–benzene (89 : 11 v/v) is stable even at 30 atm. oxygen pressure (Fig. 1e).

FIG. 1.

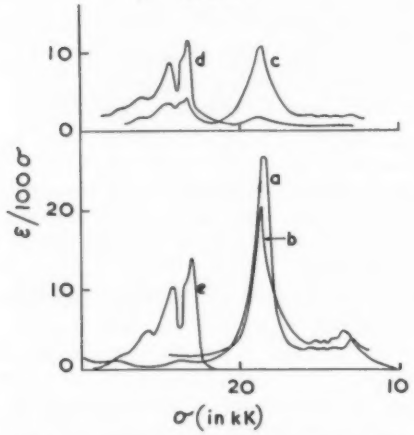

FIG. 2.

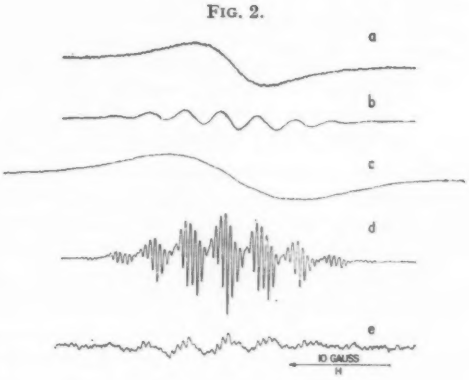

FIG. 1. *Absorption spectra* (20°) *of perylene in*: (a) $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (29 *mole % of complex*) *after contact with air*; (b) $CF_3{\cdot}CO_2H{-}C_6H_6$ (89 : 11 v/v) *at 4 atm. oxygen pressure*; (c) $CF_3{\cdot}CO_2H{-}AcOH{-}C_6H_6$ (57 : 32 : 11 v/v) *at 60 atm. oxygen pressure*; (d) $CF_3{\cdot}CO_2H{-}AcOH{-}C_6H_6$ (57 : 32 : 11 v/v) *after contact with oxygen* (60 *atm.*) *and expansion*; *and* (e) $AcOH{-}C_6H_6$ (89 : 11 v/v) *at* 30 *atm. oxygen pressure.*

FIG. 2. *Derivatives of electron-spin resonance spectra of perylene in*: (a) HF *at* 20° *after contact with air*: (b) $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (40 *mole % of complex*) *at* 20° *after contact with air*; (c) *in* $CF_3{\cdot}CO_2H$ *after contact with air*; (d) *in* 98% H_2SO_4; *and* (e) *in* $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (40 *mole % of complex*) *at* −30° *after contact with air.*

The formation of this ion was quantitatively studied in trifluoroacetic–acetic acid–benzene (57 : 32 : 11 v/v). In this medium perylene dissolves as a molecule and high oxygen pressures are needed to convert it into its monopositive ion (Fig. 1c).*

The formation of the positive ion from perylene and oxygen is rapid. The absorption spectra of the solutions slowly change, the absorption bands of the molecule as well as of the positive ion decreasing in intensity. After lowering of the pressure to 1 atm. the solutions mainly display the absorption bands of the molecule (Fig. 1d). When this procedure was performed rapidly, at least 85% of the perylene initially dissolved could be recovered. The results are summarized in Table 1. The concentration of the positive ion has been taken as the difference between the concentration of molecule present initially and after admission of oxygen, as calculated from the absorption spectrum.

Electron-spin Resonance Spectra.—The electron-spin resonance spectra of perylene, dissolved in anhydrous $HF{-}CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (40% of complex) and trifluoroacetic acid after contact with air, as well as in sulphuric acid, are given in Fig. 2. The hyperfine structure of the perylene

* Benzene was added to the acidic solvent to dissolve perylene to a sufficient extent. This has the disadvantage of lowering the molar extinction coefficients of the bands of the positive ion somewhat (cf Figs. 1a and b).

TABLE 1. *Concentration of molecule* [M] *and positive ion* [M⁺] *and the ratio* [M⁺]/[M] *in a solution of perylene in* $CF_3 \cdot CO_2H$–AcOH–C_6H_6 (57 : 32 : 11 *v/v*) *at* 20° *and various oxygen pressures.*

(Concns. are 10^{-4} mole $l.^{-1}$.)

p (atm.)	[M]	[M⁺]	[M⁺]/[M]	*p* (atm.)	[M]	[M⁺]	[M⁺]/[M]	*p* (atm.)	[M]	[M⁺]	[M⁺]/[M]
0	1·09	0·11	0·10	30	0·40	0·80	2·00	80	0·20	1·10	5·50
9½	0·66	0·54	0·82	36	0·37	0·83	2·24	85	0·21	1·09	5·20
12	0·60	0·60	1·00	43	0·35	0·85	2·43	95	0·16	1·04	6·50
18½	0·49	0·71	1·45	60	0·26	1·04	4·00	95	1·19 *	6·01 *	5·05
24	0·45	0·75	1·67								

* At this high concentration the perylene is decomposed rapidly. Only 35% of the amount initially dissolved could be recovered after elimination of the oxygen.

TABLE 2. *Electron-spin resonance spectra of the perylene positive ion in different acids.*

Fig. 2	Solvent	Shape	Total width * in gauss	Viscosity in poise	$\langle \Delta H^2 \rangle$ in gauss [2]
a	HF at 20°	One line	29	0·002	34
b	$CF_3 \cdot CO_2H$–H_2O–BF_3 (40%) at 20° c	9 lines of *ca.* 3·5 gauss each	29	0·08	35
c	$CF_3 \cdot CO_2H$ at 20°	One line	41	0·008	49
d	H_2SO_4 † at 20°	59 lines of *ca.* 0·51 gauss each	30	0·24	30
e	$CF_3 \cdot CO_2H$–H_2O,BF_3 (40%) at −30° c	59 lines of *ca.* 0·51 gauss each	30	0·45	—
—	H_2SO_4–H_3PO_4 (2 : 3 v/v) at 55° c	59 lines of *ca.* 0·51 gauss each	30	0·15	—
—	H_2SO_4–H_3PO_4 (2 : 3 v/v) at 20·5° c	45 lines of *ca.* 0·51 gauss each	25	0·52	—
—	H_2SO_4–H_3PO_4 (2 : 3 v/v) at −14° c	7 lines of *ca.* 3·5 gauss each	25	3·15	—

* Total width has been measured between the points where the resonance signal could just be distinguished from the noise. † The *g*-value of the ion in sulphuric acid is 2·0028.[3b]

positive ion in sulphuric acid appears to be well resolved.[3] The spectrum was measured at a micro-wave energy level considerably lower than normally applied. At higher energy saturation broadening of the hyperfine structure [4] was observed. The spectra of the perylene positive ion in the other acids were measured at the energy level used for the sulphuric acid solution. It can be seen that the shape and the width differ considerably, and that a better resolution of the hyperfine structure for perylene in $CF_3 \cdot CO_2H$–H_2O,BF_3 is obtained at −30° c (see also Table 2).

In addition, the spectrum was measured in a 2 : 3 v/v oxygen-free mixture of sulphuric and phosphoric acid at 55°, 20·5°, and −14° c (Table 2). At 55° the resolution obtained was similar to that in sulphuric acid, but at lower temperature the hyperfine structure is not fully resolved and at −14° c the spectrum resembles that of Fig. 2b. Evidently in the absence of oxygen and at high viscosities (estimated correlation time for rotation $\sim 10^{-8}$ sec.) the anisotropy of the hyperfine interaction results in a broadening of the spectrum.[5]

In highly acidic solvents of low viscosity in the presence of oxygen ($\sim 5 \times 10^{-3}$ mole $l.^{-1}$) there is again loss of hyperfine structure. This is attributed to exchange between oxygen and the perylene positive ion.[5,6,7] The exchange interaction becomes less at higher viscosities, as can be seen by comparing Figs. 2a, b, and e.

DISCUSSION

Evans [8] has shown that in chloroform weak complexes are formed between oxygen or nitric oxide and aromatic hydrocarbons. These complexes display well-defined absorption

[3] (*a*) de Boer and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 4549; (*b*) de Boer, Thesis, Free University, Amsterdam, 1958; (*c*) Carrington, Dravnieks, and Symons, *J.*, 1959, 947.
[4] Lupinski, Thesis, Leiden, 1959.
[5] Pake and Tuttle, jun., *Phys. Rev. Letters*, 1959, **3**, 423.
[6] Deguchi, *J. Chem. Phys.*, 1960, **32**, 1584.
[7] Hausser, *Naturwiss.*, 1960, **47**, 251.
[8] Evans, *J.*, 1957, 1351, 3885.

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bands of the singlet–triplet transitions of the hydrocarbons. The optical density is approximately proportional to the oxygen pressure, which suggests the reaction

$$M + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M,O_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

Hoijtink [9] explained these singlet–triplet transitions on the basis of exchange interaction in the complexes. That these weak complexes may have a certain stability is clear from the charge-transfer-type absorption bands observed.

Our results show that greater acidity of the solvent favours electron-transfer, leading

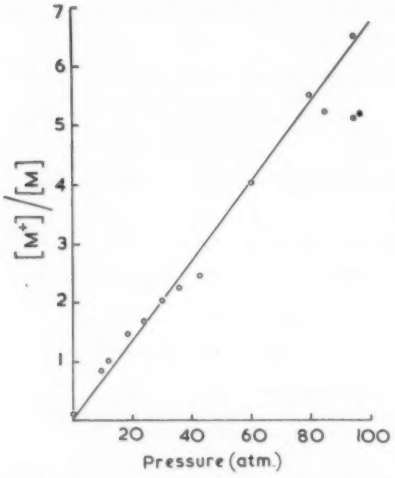

FIG. 3. *Ratio* $[M^+]/[M]$ *as a function of the oxygen pressure for perylene in* $CF_3{\cdot}CO_2H$–AcOH–C_6H_6 (57 : 32 : 11 v/v). (*For point marked* * *see footnote to Table* 1.)

to the formation of the positive ions M^+. In solvents of relatively low acidity our results are consistent with the reaction

$$M + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^+{\cdot}O_2^- \quad \ldots\ldots\ldots\ldots \quad (2)$$

in other words, with an electron-transfer in the complex M,O_2:

$$M,O_2 \rightleftharpoons M^+{\cdot}O_2^- \quad \ldots\ldots\ldots\ldots \quad (3)$$

In solvents of higher acidity and higher dielectric constant, for example, anhydrous hydrogen fluoride, the complex will dissociate and probably give rise to hydrogen peroxide:*

$$2M + O_2 + 2HF \rightleftharpoons 2M^+ + 2F^- + H_2O_2 \quad \ldots\ldots\ldots \quad (4)$$

It is the increase in acidity rather than an increase in dielectric constant that leads to electron transfer in M,O_2.†

Absorption Spectra.—Reaction (2) requires that the ratio $[M^+]/[M]$ should increase linearly with the oxygen pressure and be independent of the concentration of hydrocarbon. Fig. 3 shows that these requirements are met by the experimental results. The equilibrium constant, defined as

$$K' = \frac{[M^+{\cdot}O_2^-]}{[M]p} \quad \text{or} \quad K = \frac{[M^+{\cdot}O_2^-]}{[M][O_2]} \quad \ldots\ldots\ldots \quad (5)$$

* It is indeed difficult to obtain solutions of the proton complex of perylene in hydrogen fluoride because traces of oxygen will convert it into the positive ion. At atmospheric pressure of oxygen the ratio $[M]/[M^+]$ is estimated to be of the order of 10^{-7}.

† A solution of perylene in methanol at 45 atm. of oxygen did not display the bands of the positive ion.

[9] Hoijtink, *Mol. Phys.*, 1960, **3**, 67.

where p is the partial pressure of oxygen, is given by $K' = 0{\cdot}067$ atm.$^{-1}$ or $K = 5$ l. mole^{-1}. Evidently the electron-transfer complex $M^+ \cdot O_2^-$ in this medium is very weak and readily dissociates into the hydrocarbon and oxygen. The average life-time can be estimated in the following manner: the rate k_1 of reaction (1) between the uncharged partners, perylene and oxygen, will be diffusion-limited. This is consistent with the observation that the quenching by oxygen of the fluorescence of aromatic molecules in acetic acid is diffusion-limited. If we assume that the electron-transfer of reaction (3) is fast, the rate constant k_2 of reaction (2) is also diffusion-limited and therefore of the order of 10^{10} sec.$^{-1}$ l. mole^{-1}. Thus, since the equilibrium constant $K = 5$ l. mole^{-1}, the rate constant k_{-2} must be approximately equal to 10^9 sec.$^{-1}$, which means that the average life-time of the complex is of the order of 10^{-9} sec. If, however, the electron-transfer is slow, or if it only occurs when the aromatic molecule and the oxygen molecule are in a particular conformation, the average life-time will be greater.

The values of the constant K for various acid mixtures given in Table 3 illustrate the influence of the acidity. In trifluoroacetic acid the average life-time of the complex must be $\sim 10^{-7}$ sec. if one assumes the reaction to be diffusion-limited.

TABLE 3. *Values of the equilibrium constant K (l. mole^{-1}) of reaction (2) for various acid mixtures at 20°.*

Composition (v/v) of acid mixture	K	Composition (v/v) of acid mixture	K
$CF_3 \cdot CO_2H$–C_6H_6 (89 : 11)	$\sim 10^3$	$CF_3 \cdot CO_2H$–AcOH–C_6H_6 (70 : 19 : 11)	$\sim 4 \times 10^2$
AcOH–C_6H_6 (89 : 11)	$< 2 \times 10^{-2}$	,, ,, (57 : 32 : 11)	5
		,, ,, (44·5 : 44·5 : 11)	$\sim 2 \times 10^{-1}$

Electron-spin Resonance Spectra.—The question arises if one can deduce from the electron-spin resonance spectra whether electron-transfer occurs in the complex $M^+ \cdot O_2^-$, for which an average life-time of 10^{-7} sec. was calculated. For this purpose the spectra of the perylene positive ion in anhydrous hydrogen fluoride and $CF_3 \cdot CO_2H$–H_2O,BF_3 will be compared with that in trifluoroacetic acid. In the former strongly acidic solvents one does not expect electron-transfer since the complex $M^+ \cdot O_2^-$ is completely dissociated, but the exchange interaction with the oxygen molecule causes a loss of structure, which loss, in accordance with the results in Table 2, decreases with increasing viscosity.[5] For the latter process one expects the second moment $\langle \Delta H^2 \rangle$ of the spectrum to be approximately constant. Table 2 shows this to be the case. If the argument of Pake and Tuttle[5] is used, the line width of 7·6 gauss of the spectrum in hydrogen fluoride (Fig. 2a) leads to a frequency of the phase-interrupting collisions between oxygen and the perylene positive ion of 10^7 sec.$^{-1}$. This value may be compared with the frequency of collisions between proton complexes and oxygen in hydrogen fluoride that produce quenching of the fluorescence of the former. The frequency of these collisions under comparable conditions was found[10] to be 5×10^7 sec.$^{-1}$, from which it appears that the exchange process is efficient.

The second moment of the spectrum of a solution in trifluoroacetic acid is significantly greater: 49 gauss^2 as compared with 35 gauss^2. This broadening of the spectrum can be interpreted as caused by an electron-transfer in the complex at a rate of about 10^7 sec.$^{-1}$, which agrees with the estimate given above.

In strongly acidic solvents one expects oxygen to form hydrogen peroxide according to reaction (4). In accordance with this, the electron-spin resonance spectra of these solutions give no indication of any other paramagnetic particle. Further the hyperfine structure of the spectrum of the perylene positive ion in these solutions is much better resolved when the frequency of the phase-interrupting collisions between oxygen and the perylene positive ion is decreased by increasing the viscosity, *e.g.*, in a solution of $CF_3 \cdot CO_2H$–H_2O,BF_3 at −30° c (Fig. 2e). Therefore, in the direct neighbourhood of the perylene positive ion dissolved in a strong acid there cannot be another paramagnetic particle with which the ion could frequently interact.

[10] Mackor and Gaaf, unpublished results.

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In the weakly acidic solvents oxygen is expected to form O_2^- in the ion pair $M^+ \cdot O_2^-$. Apparently the line width of its spectrum is so great that it is not observed. It may be noted that the spectrum of radicals produced from a hydrogen peroxide glass and attributed to $HO_2 \cdot$ has a line width of about 100 gauss.[11] Bennett *et al.*[12] found that the spectrum of O_2^- in superoxide is even very much wider.

In conclusion, our results indicate that in acidic solvents aromatic hydrocarbons may react with molecular oxygen to form the hydrocarbon monopositive ion. In relatively weak acids the reaction takes place by an electron-transfer in the weak complex M,O_2 (eqn. 2). The ease of transfer depends primarily on (*a*) the ionization potential of the molecule, which is very low for perylene, and (*b*) the stabilization of the complex by interaction with the protons of the acid HZ. Our results give no information whether the acid transfers a proton to the O_2^- ion in the complex $M^+ \cdot O_2^- (M + O_2 + HZ \rightleftharpoons M^+ \cdot O_2HZ^-)$ or whether the complex $M^+ \cdot O_2^-$ is stabilized by solvation by the acid.

The authors thank Dr. C. Maclean and Dr. M. S. de Groot for valuable discussions and for assistance with the electron-spin resonance measurements.

Koninklijke/Shell-Laboratorium, Amsterdam,
Shell Internationale Research Maatschappij N.V. [*Received, September* 12*th*, 1960.]

[11] Livingston, Ghormley, and Zeldes, *J. Chem. Phys.*, 1956, **24**, 483; Gibson, Symons, and Townsend, *J.*, 1959, 269.
[12] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443.

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190. *The Reduction of Symmetrical* 1,2- *and* 1,3-*Diketones with Sodium Borohydride, and the Separation of Diastereoisomeric* 1,2- *and* 1,3-*Diols by Means of Borate Complexes.*

By Johannes Dale.

Acyclic, but not cyclic, 1,3-diketones can be reduced with sodium borohydride to the corresponding 1,3-diols in excellent yield if their acidic properties are ignored. In the form of their sodium salts no reduction takes place. In general, the *meso*-diol is the main product, and its formation is favoured by working at low temperature and with dilute solutions. 1,2-Diketones also give one isomer as the predominant product but, depending on the structure, it can be either the *meso*- or the racemic diol.

A method of separating acyclic diol isomers, based on the fact that *meso*-1,3-diols and racemic 1,2-diols form complexes with sodium borate, has been worked out. It is particularly well suited in connection with reduction of diketones by sodium borohydride as the complexes are formed directly.

Boric esters of some of the diols have been isolated.

A new case of resolution of a racemate by spontaneous crystallization has been observed (1,3-diphenylpropane-1,3-diol).

The reduction of some 1,2-diketones with sodium borohydride was reported in 1949 by Chaikin and Brown,[1] but only incomplete data were presented with regard to the steric course of this reduction. The sole mention made of 1,3-diketones by these authors was a note on an unsuccessful attempt to reduce acetylacetone; only propan-2-ol was isolated, a result of hydrolysis and subsequent reduction of the acetone so formed.

We have now found that the reduction to the diol fails only when the acyclic 1,3-diketones, which are weakly acidic, are completely neutralized before reaction, presumably because of electrostatic repulsion between the enolate ion and the borohydride ion. If the acidic properties are simply ignored, the reduction proceeds rapidly and in excellent

[1] Chaikin and Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 122.

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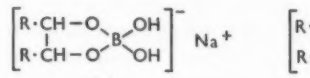
yield; no by-products can be isolated, and the sodium borohydride decomposes only slowly. In fact, the reduction of acyclic 1,3-diketones by sodium borohydride seems to constitute the best method available for the preparation of the corresponding 1,3-diols. Compared with catalytic hydrogenation [2] and reduction by lithium aluminium hydride,[3] it has the advantage that there is no loss of oxygen or formation of unsaturation. However, cyclic 1,3-diketones are more strongly acidic and decompose the borohydride before reduction can take place.

It seemed of interest to establish how strong an acid has to be to decompose the borohydride instead of being reduced. Since dimedone, with pK_a 5·17, was not reduced at all, but decomposed sodium borohydride violently, and acetylacetone, with pK_a 8·94,[4] was easily reduced, the limiting pK_a had to be between these values. The gap was narrowed by the finding that cyclopentane-1,2-dione (pK_a 8·75) and the triketone diacetylacetone [4] (pK_{a1} 7·42) could be smoothly reduced. [It is also interesting that monosodium maleate (pK_{a2} for maleic acid 6·5), although no ketone and although it decomposed the borohydride, apparently was partially reduced, since maleic acid could not be completely recovered but contained some strongly smelling unidentified substance, presumably γ-hydroxycrotonic acid or its lactone.]

Although the reduction of acyclic 1,2- and 1,3-diketones and cyclic 1,2-diketones thus proceeds excellently, isolation of the diols presented a problem in some cases, as a variety of boron-containing products of the general types (I—IV) were encountered, and at first made it difficult to free the diol from boron.

Of these compounds the sodium borate complexes (I and II) are formed under alkaline conditions; very often the compounds (I) can be isolated crystalline from water; they will be described in more detail in the following paper. The boric esters of the types (III) (or its anhydride) and (IV) are formed under neutral or acidic conditions. There is a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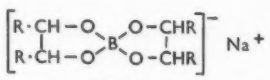
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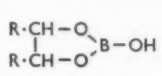
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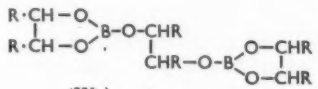
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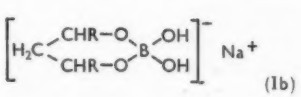
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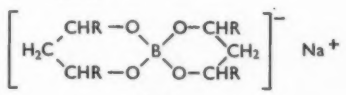
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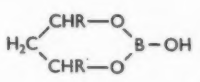
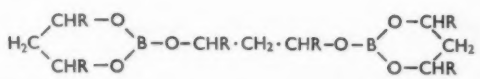

(IIIb)


(IVb)

notable difference in hydrolytic stability between the five-membered and the six-membered ring in these boric esters, the former being the less stable although forming the more stable complexes (see Experimental section and the two following papers). As is to be expected, the compounds (I and III) are formed when sodium borate or boric acid is in excess; (II and IV) when the diol is in excess.

[2] Sprague and Adkins, *J. Amer. Chem. Soc.*, 1934, **56**, 2669.
[3] Dreiding and Hartman, *J. Amer. Chem. Soc.*, 1953, **75**, 3723.
[4] Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1162.

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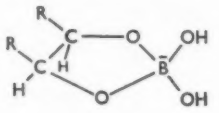
Special procedures had to be developed to isolate the pure diols; these were turned to an advantage when it was observed that the formation and stability of the alkali borate complexes and the boric esters depended on the steric configuration of the diols and thus afforded a means of separating the symmetrical diols into the *meso*- and racemic forms (potentially also unsymmetrical diols into the racemic *erythro*- and *threo*-forms).

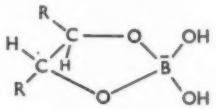
The general procedure, which had to be modified in some cases, consists in evaporating the alkaline reaction mixture, or a prepared mixture of the diols and excess of sodium metaborate, to dryness, and extracting the isomer which does not form a complex from this residue with a solvent, generally chloroform or ether. Then the extracted residue is dissolved in water, wherefrom the other isomer can then be extracted. As the hydrolysis equilibrium is continuously displaced during extraction, it is, at least for 1,3-diols, in general not necessary or advisable to acidity the alkaline solution, since then a mixture of the diol and the cyclic ester (III) may be obtained which, if distilled, forms the trisdiol diborate ester (IV). That the structure of esters of this type, which can also be formed directly from the diol and boric acid, is as shown (IV), and not of the " triple-bridge " or " cage " type suggested by Dupire,[5] could be demonstrated by the fact that tri(pentane-2,4-diol) diborate (IVb; R=H) is partially hydrolysed even by atmospheric humidity to give 1 mol. of diol and 2 mol. of the cyclic diol monoborate (IIIb), which, in contrast, is so stable against further hydrolysis that it can be extracted unchanged from aqueous solution.

In some cases when the complex is very stable, especially in the case of 1,2-diols, it is not necessary to evaporate the solution before extracting the uncomplexed isomer. In other cases care must be taken that the evaporation is not carried too far, because the anhydrous complexes may be soluble in the solvent used to extract the free diol; this happens most frequently when the groups R are large hydrocarbon groups, or when the diol is present in excess so that complexes of the type (II) are formed. The difficulty may be avoided by using benzene or hexane as extracting solvent.

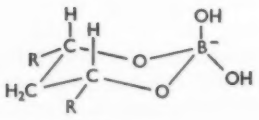
Whereas the 1,3-diol complexes (Ib) are usually sufficiently hydrolysed in water to allow the liberation of the diol by repeated extractions, the 1,2-diol complexes (Ia) are much more stable, and sometimes necessitated special procedures. Usually, the following method proved satisfactory: The alkaline solution was first extracted a few times to remove a reasonable part of the diol, then acidified, and the mixture of the remaining diol and its cyclic ester (IIIa) was next extracted completely; when this mixture was again dissolved in aqueous alkali, the net result was a reduction of the borate content, and a new crop of pure diol was extracted; this process was repeated as necessary. A very efficient method of removing most of the boric acid was to treat the extracted liquid



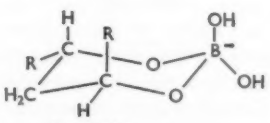
meso



Racemate



meso



Racemate

mixture of a water-soluble diol and its boric ester with the calculated quantity of water needed to hydrolyse the boric ester; the precipitated boric acid was then filtered off, and

[5] Dupire, *Compt. rend.*, 1936, **202**, 2086.

the product treated with alkali as above. If too much water was used, the boric acid dissolved, and the initial mixture was obtained on extraction. In some cases an excess of a strong complex-former, such as mannitol, can be added to liberate the diol from the alkaline solution. These methods proved much more simple and efficient than other proposed methods to eliminate boron from strong complexes, *e.g.*, its removal as methyl borate,[6,7] which is slow and tedious. However, when R represented the very bulky t-butyl group the hydrolytic stability of the complex as well as of the cyclic ester was so high that all methods failed to liberate the racemic 1,2-diol.

The question as to which isomer in a set would form the most stable complex could be predicted by considering the steric effects of the substituents R on the ring systems. Since the five-membered ring must be essentially planar, the *meso*-1,2-diol borates will have the substituents in close approach on the same side of the ring, hence must be unstable; the racemic 1,2-diol borates would be more stable, having the substituents on opposite sides.

In the six-membered ring the steric situation is probably similar to that in cyclohexane. In the *meso*-1,3-diol borates, therefore, both substituents come on the same side and can occupy the unhindered equatorial positions to form a stable ring system, whereas in the racemic 1,3-diol borates only one substituent can become equatorial, while the other one has to be axial and will come rather close to a hydrogen atom and to a hydroxyl group.

That the effect depends on the bulkiness of the substituent, is well demonstrated by the fact that when R is phenyl the separation is satisfactory under varying conditions, whereas when R is methyl both isomers form alkali-borate complexes although their stabilities differ. The stability difference is sufficient in the case of butane-2,3-diol to allow an easy separation of the isomers if complete evaporation of the complex mixture is avoided. In the case of pentane-2,4-diol only a partial separation can be achieved by using an insufficient amount of sodium borate, and in general the recently reported

TABLE 1. *Reduction of diketones with sodium borohydride.*

Diketone reduced	Diol formed	Temp.	Solvent	Yield of diol (%) *meso*	Yield of diol (%) racemate	More stable or only complex with
Acetylacetone	Pentane-2,4-diol	15°	Aq. MeOH	90	2	*meso*
2,2,6,6-Tetramethyl-heptane-3,5-dione	2,2,6,6-Tetramethyl-heptane-3,5-diol	20	MeOH	60	16	rac. (!)
Dibenzoylmethane	1,3-Diphenylpropane-1,3-diol	20	MeOH	52	36	*meso*
		5	MeOH *	31	11	
		20	MeOH, dilution *	47	11	
		6	MeOH, dilution	59	18	
Biacetyl	Butane-2,3-diol	15—20	Aq. MeOH	40	50	rac.
Bipivaloyl	2,2,5,5-Tetramethyl-hexane-3,4-diol	30—35	MeOH	62	3	rac.
Benzil	Hydrobenzoin	40—45	MeOH	70	12	rac.
		10—15	MeOH	81 (*cis*)	11 (*trans*)	
Cyclohexane-1,2-dione	Cyclohexane-1,2-diol	20—25	H_2O	28	30	*meso* (*cis*)
		6—10	H_2O	11	64	
Cyclopentane-1,2-dione	Cyclopentane-1,2-diol	20—35	H_2O	26	61	*meso* (*cis*)

* The low total yield is due to the addition of too much alkali.

chromatography of borate complexes on ion-exchange columns [8,9] is preferable, although it is slow and less suitable for large quantities.

The relative stabilities of the borate complexes of isomeric cyclic 1,2-diols have already

[6] Abdel-Akher, Hamilton, and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 4691.
[7] Reid and Siegel, *J.*, 1954, 520.
[8] Khym and Zill, *J. Amer. Chem. Soc.*, 1952, **74**, 2090.
[9] Nagai, Kuribayashi, Shiraki, and Ukita, *J. Polymer Sci.*, 1959, **35**, 295.

been extensively studied by Böeseken and his pupils.[10-15] In the case of the cyclohexane 1,2-diols, as expected, it is the *cis*-isomer (*meso*) which forms the most stable complex, but it is still surprisingly unstable when compared with the well-known and very stable *cis*-cyclopentane-1,2-diol complex. Derx [11] has offered an explanation in terms of the small number of molecules in " dynamic equilibrium," which have the hydroxyl groups in the right position (as in cyclopentane-1,2-diol) to form a planar five-membered ring with boric acid, but it might just as well be understood by considering the steric strain in the molecule itself; the five-membered heterocyclic ring can only become planar if the cyclohexane ring is forced into the unfavourable boat-form, and the cyclohexane ring can only assume the stable chair-form if the five-membered ring becomes skew.

Although compounds of diols with boric acid of the types (I—IV) have been isolated before,[5,11-19] and the effect of the addition of diols on the conductivity and acidity of boric acid solutions has been studied extensively and used to establish steric configurations,[10,11,15,20-23] especially of cyclic diol pairs, these compounds do not seem to have been utilized for the actual separation of isomers, except in the case of 1-methylcyclohexane-1,2-diol.[12] However, even for this diol no experimental details were given. For cyclic diols another method of separation is also available as only the *cis*-compounds form cyclic acetals with acetone,[11,12,15,21,24] but the main shortcoming is here that the hydrolysis of the acetal to liberate the diol is often accompanied by isomerization or decomposition.[12,21,24] In the acyclic series both *meso*- and racemic forms generally give isopropylidene compounds.[21]

It should be noted that many of the compounds studied by us have only slight effect on the conductivity and acidity of boric acid; and in some cases there is little difference within an isomeric pair.[10,11] Thus, Böeseken's method is actually a relatively coarse tool for structural chemical problems, compared with the sensitivity of the present separation, the reason being that hydrolysis of the complex and displacement of the hydrolysis equilibrium during extraction are prevented by removing the water.

The steric course of the sodium borohydride reduction was at first thought to be connected with the borate-complex stability, since in the first example studied, namely, acetylacetone, the resulting pentane-2,4-diol gave a stable complex and reacted with boric acid to give almost quantitatively a single crystalline stable compound of the type (IIIb), m. p. 85°. The pure isomers in this set have only recently been described,[9] but their configurations were not determined. As will be shown below, there cannot be much doubt that it is the *meso*-form which is obtained. Pentane-2,4-diol from other sources (catalytic hydrogenation) was later shown to give a smaller yield of the high-melting ester, together with lower-melting fractions which contained also the ester of the other isomer, which, when pure, melts lower (37°) than any of these mixtures.

For other diketones there is no such general correlation between steric course and complex stability, as can be seen from Table 1. First, the reduction is less stereospecific; then, 1,2-diketones give as main reduction product in general the isomer which does not form a borate complex.

[10] Böeseken and van Giffen, *Rec. Trav. chim.*, 1920, **39**, 183.
[11] Derx, *Rec. Trav. chim.*, 1922, **41**, 312.
[12] Böeseken (and Maan), *Ber.*, 1923, **56**, 2409.
[13] Hermans, *Proc. Roy. Acad. Amsterdam*, 1923, **26**, 32.
[14] Hermans, *Z. anorg. Chem.*, 1925, **142**, 83.
[15] Maan, *Rec. Trav. chim.*, 1929, **48**, 332.
[16] Pastureau and Veiler, *Compt. rend.*, 1936, **202**, 1683.
[17] Rippere and LaMer, *J. Phys. Chem.*, 1943, **47**, 204.
[18] Morell and Lathrop, *J. Amer. Chem. Soc.*, 1945, **67**, 879.
[19] Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5497.
[20] Böeseken, *Ber.*, 1913, **46**, 2612.
[21] Hermans, *Z. phys. Chem.*, 1924, **113**, 337.
[22] Lees, Fulmer, and Underkofler, *Iowa State Coll. J. Sci.*, 1944, **18**, 359.
[23] Knowlton, Schieltz, and Macmillan, *J. Amer. Chem. Soc.*, 1946, **68**, 208.
[24] Hermans, *Ber.*, 1924, **57**, 824.

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Table 1 shows also that lowering the temperature and increasing the dilution, in the cases so far studied, make the reduction more stereospecific. It is not quite clear what conclusions may be drawn with regard to the reaction mechanism, especially since they will depend on what conformation is assumed for the acyclic diketones in solution and

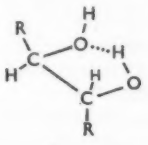
TABLE 2. *Physical properties of isomeric diols.*

Diol	OH infrared band		Melting point	
	meso	Racemate	*meso*	Racemate
Pentane-2,4-diol	Double [9]	Double [9]	Liquid	52—53° [9]
2,2,6,6-Tetramethylheptane-3,5-diol	Single	Double	99—100°	174
1,3-Diphenylpropane-1,3-diol	Single	Double	108—109	130
Butane-2,3-diol	Double [a,b]	Double [a,b]	34 [d]	7 [d]
2,2,5,5-Tetramethylhexane-3,4-diol	Single [b]	Double [b]	123	—
1,2-Diphenylethane-1,2-diol	Single	Double	136—137	119—120
	(*cis*)	(*trans*)	(*cis*)	(*trans*)
Cyclohexane-1,2-diol	Double [a,c]	Single [a,c]	98	104
Cyclopentane-1,2-diol	Double [a,c]	Single [a,c]	29—30 [11]	55

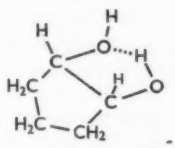
[a] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492. [b] *Idem, ibid.*, 1958, **80**, 5950. [c] *Idem, ibid.*, 1954, **76**, 4323. [d] Wilson and Lucas, *ibid.*, 1936, **58**, 2396.

since it is not known whether both carbonyl groups are reduced simultaneously by the same borohydride anion or in a clear two-step reaction, as indicated in the case of benzil (see p. 920).

Some physical properties of the isomeric diols have been compiled in Table 2. The assignment of configuration to the sets for which the racemate has not been resolved are based on the behaviour towards boric acid. Additional support comes from a comparison of the melting points, which show striking regularities. Thus, among acyclic 1,3-diols it is always the racemate which is the higher melting; among acyclic 1,2-diols it is the *meso*-form. In pentane-2,4-diol the assignment is also supported by the fact that the cyclic borate of the *meso*-form, which has the higher symmetry, is the higher-melting.*



Racemate



cis

The OH stretching absorptions in the infrared region likewise reveal regularities. It has already been shown by Kuhn [25-27] that the acyclic racemic 1,2-diols and *cis*-cyclopentane-1,2-diol show a double band because of internal hydrogen bonding, leading to non-equivalent hydroxyl groups, whereas *meso*-diols (with large R groups) and *trans*-cyclopentane-1,2-diol can only form equivalent external hydrogen-bonds, or remain non-bonded in dilute solution, and therefore show a single hydroxyl band. By similar reasoning one would expect that in acyclic 1,3-diols only the *meso*-form should form an internal hydrogen bond and should give a doublet in the hydroxyl region if the ring which is formed has to be non-planar. Instead it is observed that also here it is the racemate which has a doublet and the *meso*-form which shows a single hydroxyl band. A possible explanation is that the hydrocarbon skeleton does not form the supposed planar zig-zag stretched-out

* Further support has been obtained by Dr. J. F. M. Oth (personal communication) from the nuclear magnetic resonance spectra of the two borates.

[25] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.
[26] Kuhn, *J. Amer. Chem. Soc.*, 1954, **76**, 4323.
[27] Kuhn, *J. Amer. Chem. Soc.*, 1958, **80**, 5950.

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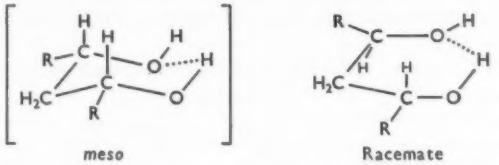
chain, but is helically twisted, as in many polymers with 1,3-substituents along a hydrocarbon chain, thereby making the ring approximately planar:



meso Racemate

With bulky R groups, therefore, only the racemate should be capable of forming the internally hydrogen-bonded ring-structure.

When R is t-butyl, that is in 2,2,6,6-tetramethylheptane-3,5-diol, another abnormality was noted. The separation method worked well, but surprisingly in the reversed sense, although the behaviour towards boric acid itself was normal inasmuch as only the *meso*-isomer formed an ester. The reason may be that the t-butyl groups are so bulky that none of the isomers can form a cyclic compound when there is an extra hydroxyl group on the boron atom, as is the case in the complex. On the other hand, the racemate may form more easily a polymer with sodium borate, which may be preferentially stabilized by the shielding effect of the big groups.

Finally it should be mentioned that in the case of 1,3-diphenylpropane-1,3-diol [2,3,28] only the higher-melting racemic isomer has earlier been obtained pure, and reported attempts to isolate the *meso*-form have failed (reported m. p. of isomer mixture 94—98°). This mixture could easily be separated by the borate method into the pure isomers. On the other hand, it was observed that the racemate, m. p. 130°, sometimes contained crystals which remained unmelted up to 150°, close to the melting point of each of the antipodes.[29] Obviously, one had to do with one of the rare cases when optical resolution occurs spontaneously by crystallization. By slow evaporation of methanol solutions at room temperature, crystals were obtained which separately melted at 152°. They had no typical left- or right-handed shape allowing sorting by handpicking, but the optical activity of the biggest ones could be measured separately in solution and showed either positive or negative rotation. However, the rotation was much lower than reported for the pure antipodes,[29] so evidently the big crystals are conglomerates.

We have here the strange case of an isomer set, in which the *meso*-form cannot be separated from the racemate by crystallization, although the racemate itself can be resolved spontaneously by crystallization.

Experimental

Reduction of Acetylacetone.—In a typical experiment acetylacetone (20 g.) in methanol (50 ml.) was dropped slowly into a stirred solution of sodium borohydride (5 g.) and sodium hydroxide (0·1 g.) in water (50 ml.). The reaction is exothermic and the temperature was kept below 20°. Then the mixture was left overnight or refluxed for 20 min. (Alternatively the sodium borohydride was added to the acetylacetone solution.) The methanol was distilled off and, on cooling, crystals were obtained. On further concentration and crystallization a total of about 30 g. may be obtained. The substance easily loses water but does not melt. Extraction of this solid sodium borate complex with chloroform yielded no material.

If the complex is dissolved in 2N-sulphuric acid and the neutral or acid solution extracted with chloroform, a liquid is obtained which on distillation gives a boron-free fraction, b. p. 201°/760 mm., 98°/10 mm., n_D^{24} 1·4335 (pentane-2,4-diol), and another fraction, b. p. 300—310°/760 mm., 190°/13 mm., n_D^{24} 1·4355. The latter compound is a very viscous oil, contains boron, can be titrated by alkali, and has no infrared OH absorption, and so must be the

[28] Zimmerman and English, *J. Amer. Chem. Soc.*, 1954, **76**, 2285.
[29] Stühmer and Frey, *Arch. Pharm.*, 1953, **286**, 26.

tri(*pentane*-2,4-*diol*) *diborate* (Found: C, 54·6; H, 9·2; B, 6·6. $C_{15}H_{30}B_2O_6$ requires C, 54·9; H, 9·2; B, 6·6%). In humid air, or on addition of water, it hydrolyses, and needle-shaped crystals separate. These recrystallized from benzene–light petroleum as prisms, m. p. 82—83°, and were identified as *meso*-pentane-2,4-diol borate [9] (Found: C, 46·3; H, 8·8; B, 8·2. Calc. for $C_5H_{11}BO_3$: C, 46·2; H, 8·5; B, 8·3%); they show infrared OH absorption. The monoborate is also obtained directly by treating one mol. of diol with one mol. of boric acid. Likewise, when two mol. of the monoborate are treated with one of the diol, the high-boiling trisdiol diborate is formed.

The most efficient method of isolating the diol free from borates consisted in concentrating the initial reaction mixture or dissolving the alkali borate complex in a small quantity of water and extracting it a reasonable number of times with chloroform, that is, until about half of the diol is obtained. Then the solution is acidified and extracted to give a mixture of the diol and the monoborate. This mixture is then treated with alkali, and the alkaline solution thus obtained has a lower borate content and can be extracted again to yield a new crop of pure diol. If the procedure is repeated several times the total yield of pentanediol surpasses 90% and it can be practically completely converted into the high-melting boric ester, which is the *meso*-form (see discussion).

When acetylacetone in the form of its sodium salt is treated with sodium borohydride, no reaction takes place: the temperature remains constant even if the whole portion is added at once. However, the diketone is slowly hydrolyzed to acetone and acetate, and after storage overnight a nearly quantitative yield of propan-2-ol can be obtained.

Attempts to separate the Pentane-2,4-*diol Isomers*.—An isomeric mixture, b. p. 86—88°/5 mm., of pentane-2,4-diols was obtained by catalytic hydrogenation of acetylacetone over Raney nickel at 100°/(initial)136 atm. in 83% yield. The crude boric ester was prepared and melted in the range 60—70°. Partial separation of this borate mixture was achieved by fractional crystallization from hexane, but was very slow and tedious. The diol mixture was also treated with an excess of sodium metaborate in water, and the water evaporated, but nothing could be extracted from this solid with chloroform. Apparently, in this system both isomers form a complex.

If an insufficient amount of sodium borate is used, the excess of diol can be extracted if the evaporation is not complete, but if the water is removed completely, the chloroform-soluble " spiro "-complex (IIb) is extracted. It can be prepared by mixing calculated quantities of the components, and is precipitated slowly from a concentrated chloroform solution. It is an amorphous solid and does not melt below 350°. It burns in a flame to leave a white residue. The expected amount of sodium chloride was precipitated when dry hydrogen chloride was bubbled into a chloroform solution of this complex.

When the original diol mixture was left for a week at room temperature, it crystallized partly. After another week at 0° about 8% had crystallized and was-filtered off. This crude racemic diol had m. p. 40—47° (reported [9] m. p. 52—53°) which could not be raised further by recrystallization from benzene–carbon disulphide. As with the *meso*-diol, the cyclic borate of the racemic diol can be prepared simply by mixing the diol with an excess of boric acid in a little water and extracting the product with chloroform. After recrystallization from very little hexane at 0° the racemic pentane-2,4-diol borate melted at 40° (reported [9] m. p. 37°) (Found: C, 45·9; H, 8·6; B, 8·3. Calc. for $C_5H_{11}BO_3$: C, 46·2; H, 8·5; B, 8·3%). When the diol was esterified with boric acid by azeotropic distillation of the formed water with chloroform a liquid was obtained having b. p. 102—104°, n_D^{21} 1·4336. It contained no hydroxyl group, but all CH proton signals in the nuclear magnetic resonance spectrum were identical with those of the above ester; hence it must be racemic *pentane*-2,4-*diol borate anhydride* (Found: C, 49·45; H, 8·6; B, 8·7. $C_{10}H_{20}B_2O_5$ requires C, 49·65; H, 8·35; B, 8·95%). Addition of the calculated quantity of water to the liquid caused complete solidification, and recrystallization of the solid gave the same ester as was obtained by the first method.

Pentane-2,4-diol was also prepared from aldol in a Grignard reaction with methylmagnesium iodide in 20% yield. The m. p. of the boric ester from this product could not be raised above 69—73° by fractional crystallization.

Reduction of 2,2,6,6-*Tetramethylheptane*-3,5-*dione*.—The 1,3-diketone (furnished by Miss J. Golaire, University of Liège) was prepared in a Claisen condensation between phenyl pivalate and pinacolone.[30] Then a methanolic solution of sodium borohydride (200 mg.) and a little

[30] Man, Swamer, and Hauser, *J. Amer. Chem. Soc.*, 1951, **73**, 901.

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sodium hydroxide (15 mg.) was dropped slowly into a stirred solution of this diketone (210 mg.) in methanol. After refluxing for 1 hr. the solution was evaporated and the residue extracted with ether. A solid (120 mg.) was obtained which recrystallized from pentane. It sublimed at 70°/0·2 mm. as needles, m. p. 99—100°, and must be one isomeric 2,2,6,6-*tetramethylheptane*-3,5-*diol* (Found: C, 69·9; H, 12·6. $C_{11}H_{24}O_2$ requires C, 70·15; H, 12·8%). The solid complex was treated with water and extracted with ether. Crystallization from hexane yielded the isomeric diol (33 mg.) as fibre-like crystals, m. p. 174° (determined in a sealed capillary owing to sublimation) (Found: C, 70·0; H, 12·7%).

The higher-melting isomer was recovered unchanged when it was evaporated with boric acid in methanol and the residue extracted with benzene, whereas the lower-melting isomer gave its borate anhydride, m. p. 130—131° after crystallization from pentane and sublimation at 100°/0·3 mm. (Found: C, 64·15; H, 10·9. $C_{22}H_{44}B_2O_5$ requires C, 64·4; H, 10·8%). Further, since the higher-melting isomer has a double infrared OH band, and the lower-melting a single band, there is no doubt that they represent the racemate and the *meso*-form respectively; that is, the separation method works in the opposite sense.

A mixture of the two isomers shows no depressed m. p., but melts at an intermediate temperature. The *meso*-form could not be obtained pure by crystallization of such mixtures.

When the diketone is hydrogenated over Raney nickel the racemate is obtained in a yield of 63% and the *meso*-form only in 4% (personal communication from Miss J. Golaire).

Reduction of Dibenzoylmethane.—A methanolic solution of sodium borohydride (1 g.) and sodium hydroxide (0·07 g.) was dropped into a stirred solution of dibenzoylmethane (9 g.) in methanol. There was little evolution of heat and the mixture was refluxed for 2 hr.

If the solution is neutralized or acidified, the methanol removed, and the aqueous solution then extracted with ether, a semisolid is obtained which by crystallization from benzene gives racemic 1,3-diphenylpropane-1,3-diol (2·2 g.), m. p. 128—129°. The benzene mother-liquor contains boron; it can be washed free from boron with alkali, and then on evaporation provides material which by crystallization from benzene–light petroleum furnishes an inhomogeneous substance (5·7 g.), m. p. 92—97°; this cannot be further resolved by crystallization. However, when this mixture is treated with an excess of sodium metaborate in water–methanol and evaporated, and the dry residue extracted with ether, another crop of the racemic diol (1·0 g.) is obtained. The residue is then dissolved in water, and the solution extracted with ether. Crystallization from benzene gives needles (4·7 g.), m. p. 108—109°. A comparison of the infrared spectra shows that the product does not contain the racemate; hence it must be the pure meso-1,3-*diphenylpropane*-1,3-*diol* (Found: C, 79·1; H, 6·9. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·05%).

The preferred method is to evaporate the alkaline reaction mixture directly, and extract the residue to yield the racemate, whereafter the residue is dissolved in water and this solution extracted to yield the *meso*-form.

When the amount of alkali, which is added to stabilize the sodium borohydride solution, is substantially higher, the yield becomes lower and complications arise during the working-up. Thus, the sodium salt of dibenzoylmethane (yellowish needles, m. p. > 330°) and a reduced hydrolysis product, α-methylbenzyl alcohol, enter the ether together with the racemic diol. If sufficient alkali is added to neutralize the dibenzoylmethane completely, no reduction takes place, but after 2 hours' refluxing the substance is partly hydrolysed into acetophenone and benzoate, as α-methylbenzyl alcohol and benzoic acid were isolated, and only 40% of the starting material was recovered.

Whereas the total yield of diols thus seems to be determined chiefly by the amount of alkali added, a decrease of the reaction temperature, and of the concentration of both reactants, had a marked effect on the relative yields of the two isomers (cf. Table 1). A typical " high-dilution " experiment was performed as follows: A solution of dibenzoylmethane (3 g.) in methanol (200 ml.) and another solution of sodium borohydride (1 g.) and sodium hydroxide (0·1 g.) in methanol (100 ml.) were dropped slowly at the same time into 250 ml. of methanol with stirring. The products were isolated as described above.

Spontaneous Resolution of Racemic 1,3-*Diphenylpropane*-1,3-*diol.*—Crystallization from benzene or ethyl acetate or mixtures thereof yielded in general only the racemate, m. p. 130°. Occasionally, some needles melted at 150°. When a concentrated methanol solution was left overnight at room temperature in an open vessel, big crystals of the antipodes were obtained, m. p. 151·5° (lit.,[29] 152·5°). Some of them were as long as 2 cm. and weighed 800 mg. Single

crystals were dissolved separately in methanol and the specific rotation measured. For crystals weighing from 50 to 100 mg. $[\alpha]_D^{20}$ varied between 20° and 40°, positive or negative. Stühmer and Frey [29] report ±106·5°. With bigger crystals even lower values were obtained. Evidently, the bigger the crystal, the higher the probability of formation of a conglomerate.

Reduction of Biacetyl.—A solution of biacetyl (34·4 g.) in water (50 ml.) and methanol (25 ml.) was dropped slowly into a solution of sodium borohydride (10 g.) and sodium hydroxide (0·6 g.) in water (100 ml.). The temperature was kept at 15—20°. The mixture became colourless. After a short period of heating, the solution was concentrated until crystallization of the complex began, and the *meso*-butane-2,3-diol was then extracted with chloroform. The quantity corresponding to the excess of diol over sodium borate in the solution was easily extracted, but repeated extractions were necessary to remove the rest of the *meso*-diol. The product (13·8 g.) distilled at 58—60°/0·4 mm. as a viscous oil,[23] n_D^{24} 1·4372. It was identified as its di-*p*-nitrobenzoate,[31] m. p. 188—189°, obtained in 95% yield. The borate solution was then acidified and extracted with ether. A ~1 : 3 mixture (20·4 g.) of the racemic butane-2,3-diol and its borate was obtained. The free diol was isolated by treatment of the mixture with excess of concentrated sodium hydroxide solution and extraction with chloroform, whereupon the solution was again acidified and the whole process repeated to yield another crop of borate-free diol. However, the method became much more efficient if the mixture was treated with the exactly calculated quantity of water to hydrolyse the borate, and the precipitated boric acid filtered off, before the alkali treatment. (N.B. Excess of water redissolves the boric acid.) The racemic diol distilled at 176°/760 mm., had n_D^{24} 1·4318, and was identified as its di-*p*-nitrobenzoate,[31] m. p. 128°, obtained in 90% yield.

If each of the butane-2,3-diol isomers is treated with an excess of sodium borate in water, a precipitate is formed. After evaporation nothing can be extracted from the residue with chloroform.

Butane-2,3-diol Borates.—Each of the diols was treated with an excess of boric acid and the water removed by azeotropic distillation with chloroform. The *meso*-butane-2,3-diol borate anhydride distilled at 160—180°/11 mm. as an extremely viscous oil, n_D^{22} 1·4360 (cf. Morell and Lathrop [18]), indicating that the ring structure is somewhat unstable so that partial rearrangement into polymeric structures takes place in the condensed state (Found: C, 45·3; H, 8·1; B, 9·2. Calc. for $C_8H_{16}B_2O_5$: C, 44·9; H, 7·55; B, 10·1%). The racemic *butane-2,3-diol borate anhydride* distilled at 82—89°/0·7 mm. as a moderately viscous liquid, n_D^{27} 1·4233 (Found: C, 44·2; H, 7·55; B, 9·8%). Each of the borates was treated with the calculated quantity of water (one mol.) necessary to produce the simple cyclic borate, but instead the corresponding quantity of boric acid was precipitated.

Preparation of Pivaloin and Bipivaloyl.—Ethyl pivalate was prepared by heating pivalic acid (50 g.) and absolute ethanol (125 ml.) in an autoclave at 200°/25 atm. for 64 hr. in the absence of a catalyst. As the ester is very volatile with ethanol, the ethanol was not distilled, but the reaction mixture diluted with a four-fold volume of water and extracted with ether, then dried and distilled. 50·6 g. (80%) of the ester, n_D^{20} 1·3920, passed over at 118°/760 mm.

The ester was condensed with sodium [32] and gave a 60% yield of pivaloin, b. p. 85—95°/12 mm., together with a 12% yield of the yellow bipivaloyl, b. p. 55—60°/12 mm.

Bipivaloyl was also obtained by oxidation of pivaloin with chromic acid [33] in a yield of 57% (b. p. 161—170°/760 mm.).

Reduction of Bipivaloyl.—A solution of sodium borohydride (0·8 g.) in methanol containing sodium hydroxide (0·1 g.) and a little water was added dropwise to a stirred solution of bipivaloyl (3·60 g.) in methanol at 30—35°. After refluxing for 1 hr., the colourless solution was evaporated, and the solid mass extracted with benzene (ether dissolves also the complex). The benzene was evaporated and yielded the known [27] *meso*-2,2,5,5-tetramethylhexane-3,4-diol (2·13 g.), m. p. 120°, which, recrystallized from hexane, had m. p. 125°.

The residue from the benzene treatment was dissolved in 2N-sulphuric acid and extracted with ether. The ether solution slowly precipitated a solid. The ether was evaporated and the residue treated with hexane, whereby some boric acid remained undissolved. The hexane solution contained a solid (200 mg.) which, when heated first melted at 90—110°, then resolidified,

[31] Robertson and Neish, *Canad. J. Res.*, 1948, **26**, *B*, 737.
[32] *Org. Synth.*, Coll. Vol. II, p. 114.
[33] Leonard and Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388.

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and melted again at 150—151°. This substance was recrystallized from benzene–light petroleum, then having m. p. 152°. It contained boron and must be the mixed ester, *1,2-di-t-butylethylene 2-hydroxy-3,3-dimethyl-1-t-butylbutyl monoborate*,

(Found: C, 67·2; H, 11·4. $C_{20}H_{41}BO_4$ requires C, 67·4; H, 11·6%), with the racemic diol in the ring and the *meso*-diol in the side chain for the following reasons: The infrared spectrum of the solid shows a sharp band at 2·83 μ, indicating a sterically shielded, non-bonded hydroxyl group, which explains why the usual trisdiol diborate (IVb) is not formed and also the hydrolytic stability of the compound. Further, by treatment with aqueous-methanolic alkali, evaporation, and re-extraction of the residue, a crop of the *meso*-diol was obtained, while the residue after acidification yielded the cyclic racemic *2,2,5,5-tetramethylhexane-3,4-diol monoborate*, which crystallizes from hexane as needles, m. p. 98—100° (Found: C, 59·9; H, 10·6; B, 5·4. $C_{10}H_{21}BO_3$ requires C, 60·05; H, 10·6; B, 5·4%). The infrared spectrum of this ester shows a hydroxyl band at 2·98 μ.

The free racemic diol could not be extracted from an alkaline aqueous solution of its borate even in the presence of mannitol, nor could the boron be removed as methyl borate or by refluxing in humid ether (to precipitate boric acid). In some cases the m. p. of the recovered material tended to rise as much as to 120°, and estimation of the boron by titration then showed that the *anhydride* had been formed (Found: B, 5·65. $C_{20}H_{40}B_2O_5$ requires B, 5·7%).

Reduction of Pivaloin.—2,2,5,5-Tetramethylhexane-3,4-diol was also obtained in a similar reduction of pivaloin with sodium borohydride. At room temperature the yield of the *meso*-diol was 81%, of the racemic diol only 0·2%. In refluxing methanol the yield of the *meso*-form was 84%; no racemate was then isolated. As a comparison, pivaloin was reduced with lithium aluminium hydride in ether at −60° (cf. Kuhn [27]). The *meso*-diol was obtained in 80% and the racemic diol borate in 10% yield.

Attempts to isomerize meso-*2,2,5,5-Tetramethylhexane-3,4-diol to the Racemate.*—To obtain larger quantities of the racemic diol, the *meso*-diol was heated in a sealed tube with excess of boric acid in the hope that the formation of the stable borate of the racemate would favour conversion into this isomer. At 130° no change took place during 60 hr. Also after heating at 180°, the *meso*-form was recovered almost completely, together with very little (0·1%) of the mixed bisdiol monoborate (see above), m. p. 150—151°, and a volatile liquid. At 200° during 16 hr. the diol was completely converted into this liquid. The liquid had a ketonic smell and distilled at 148—150°/760 mm. The infrared spectrum showed the absence of hydroxyl groups and a strong band at 5·82 μ (ketone), hence it must be 2,2,5,5-tetramethylhexan-3-one, possibly containing some hydrocarbon (Found: C, 78·8; H, 12·7. Calc. for $C_{10}H_{20}O$: C, 76·9; H, 12·9%). When the boric acid was replaced by boron oxide, the ketone was formed already at 150°.

Reduction of Benzil.—A solution of sodium borohydride (1·5 g.) and sodium hydroxide (0·2 g.) in methanol (50 ml.) was dropped slowly into a cooled suspension of benzil (10 5 g.) in methanol (100 ml.) at 10—15°. No colour phenomena reported by Chaikin and Brown [1] were observed, only a gradual bleaching of the yellow colour of benzil. When approximately one keto-group had been reduced, the mixture consisted of a suspension of colourless crystals in a colourless liquid. On further reduction the crystals gradually dissolved. Finally, the solution was refluxed for 10 min. and left overnight.

If the reaction mixture is neutralized and worked up without utilizing the borate complex for separation, most of the hydrobenzoin (*meso*-1,2-diphenylethane-1,2-diol) crystallizes since it is the main product, but the next crystal crop melts at about 110° and is a mixture of hydrobenzoin and isohydrobenzoin (racemic 1,2-diphenylethane-1,2-diol) which is difficult to separate further by crystallization.

A quantitative separation was possible by evaporating directly the alkaline reaction mixture. In this case, however, the residue was almost completely soluble in chloroform and the extract consisted of a mixture of hydrobenzoin and the isohydrobenzoin–borate complex. When the mixture was boiled with benzene the hydrobenzoin passed into solution, from which it crystallized on cooling (8·45 g.; m. p. 136—137°). The complex was insoluble in benzene and melted with decomposition at about 220°. It was dissolved in 2N-sulphuric acid and the

solution extracted with chloroform. 1·10 g. of isohydrobenzoin were obtained, having m. p. 119—120° after recrystallization from benzene or water.

The yield of each isomer is very close to the yield obtained with lithium aluminium hydride.[34] At higher temperatures the reduction was less stereospecific (Table 1).

Reduction of Cyclohexane-1,2-dione.—A solution of sodium borohydride (2 g.) and sodium hydroxide (0·1 g.) in water (100 ml.) was dropped slowly into a stirred solution of cyclohexane-1,2-dione (6·40 g.) in methanol (100 ml.). The temperature was kept between 6° and 10°. After evaporation (the last traces of water must be carefully removed) a solid remained from which *trans*-cyclohexane-1,2-diol (4·09 g.) was extracted with chloroform (m. p. 103—104° after crystallization from benzene). The residue was dissolved in water and the solution extracted with chloroform, yielding 0·70 g. of *cis*-cyclohexane-1,2-diol, m. p. 95—97°. The mixture of these two diols was inseparable by crystallization and started to melt at 60—70°.[35]

When the reduction was conducted at room temperature, there was practically no stereospecificity (cf. Table 1).

With lithium aluminium hydride only one keto-group is reduced.[34]

The cis-*cyclohexane-1,2-diol borate* was prepared separately from 4 g. of *cis*-diol and an excess of boric acid by azeotropic distillation of the water with chloroform. On distillation the main fraction passed over at 190°/10^{-3} mm. and solidified to a glass which analysis showed to be the *anhydride* (Found: C, 54·15; H, 7·95; B, 7·9. $C_{12}H_{20}B_2O_5$ requires C, 54·2; H, 7·6; B, 8·15%). It is insoluble in carbon tetrachloride and hydrolyzed completely in water.

Reduction of Cyclopentane-1,2-dione.—Cyclopentane-1,2-dione, m. p. 52—53°, was prepared according to Dieckmann's directions.[36] A solution of the diketone (630 mg.) in water was dropped into a stirred solution of sodium borohydride (250 mg.) in water containing a little alkali. The temperature increased slowly from 20° to 35°. Finally the mixture was heated, then concentrated until crystallization began. Several extractions with chloroform yielded a total of about 390 mg. of boron-free oil which was distilled *in vacuo*; it then had m. p. 55°, hence it must be pure *trans*-cyclopentane-1,2-diol.[11] It is very hygroscopic; sublimed crystals liquefy at once when exposed to air. The remaining solid borate complex of the *cis*-diol was acidified with sulphuric acid and extracted with chloroform. About 240 mg. of a viscous oil were obtained, which is practically pure *cis*-cyclopentane-1,2-diol borate. When treated with a concentrated solution of alkali no free diol could be extracted, but after addition of a large excess of mannitol the *cis*-diol was liberated and could be slowly extracted. It distilled at 98°/9 mm. and had $n_D^{24·5}$ 1·4736.

cis-Cyclopentane-1,2-diol borate was also prepared separately from 16 g. of *cis*-diol and excess of boric acid by azeotropic distillation of the water. It distilled at 117—119°/0·5 mm., as a liquid, n_D^{15} 1·4710, which later crystallized. The m. p. 32—43°, could not be improved by recrystallization. The substance is extremely hygroscopic, and analysis shows it to be present mainly in the form of its *anhydride* (Found: C, 49·5; H, 7·1; B, 9·05. $C_{10}H_{16}B_2O_5$ requires C, 50·5; H, 6·8; B, 9·1%).

Attempts to reduce Cyclohexane-1,3-diones.—Cyclohexane-1,3-dione and 5,5-dimethylcyclohexane-1,3-dione (dimedone) rapidly decomposed the sodium borohydride and were recovered practically completely after the reaction. If the diones were used in the form of their sodium salts, no temperature rise was observed when the borohydride was added. Even after 4 hours' refluxing, the starting material could be recovered almost completely.

Preparation of Diacetylacetone.—2,6-Dimethyl-4-pyrone was prepared by treating dehydroacetic acid (70 g.) with concentrated hydrochloric acid.[37] The dimethylpyrone was then treated with barium hydroxide, and the barium salt isolated.[38] Cautious acidification of a suspension of the salt in cold water and extraction with ether yielded the triketone (28 g.), which, recrystallized from light petroleum below 40°, had m. p. 49°.

Reduction of Diacetylacetone.—A solution of sodium borohydride (8·1 g.) and sodium hydroxide (0·2 g.) in water (100 ml.) was dropped into a stirred and cooled solution of diacetylacetone (19 g.) in methanol (100 ml.). The reaction was strongly exothermic, and the solution was maintained at 20°. When about two-thirds of the borohydride had been added, further addition

[34] Trevoy and Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 1675.
[35] Svirbely and Goldhagen, *J. Phys. Chem.*, 1953, **57**, 597.
[36] Dieckmann, *Ber.*, 1894, **27**, 102, 965; 1897, **30**, 1470; 1902, **35**, 3208.
[37] King, Ozog, and Moffat, *J. Amer. Chem. Soc.*, 1951, **73**, 301.
[38] Feist, *Annalen*, 1890, **257**, 276.

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did not produce a heat effect even when the rest was added all at once. After neutralization with 4N-sulphuric acid the mixture was evaporated and the residue extracted with chloroform to yield 15 g. of a very viscous boron-containing oil. The infrared spectrum showed the presence of hydroxyl groups and the absence of carbonyl and olefin absorption. Treatment with concentrated alkali gave an insoluble amorphous, ill-defined complex. For this reason and in view of the larger number of possible isomers, no serious attempt was made to effect separation or quantitative isolation of the isomers, but the solid was extracted with ether to give a viscous boron-free *heptane-2,4,6-triol*, b. p. 128—132°/0·02 mm., n_D^{23} 1·4642 (2·3 g.) (Found: C, 56·65; H, 11·0. $C_7H_{16}O_3$ requires C, 56·7; H, 10·9%). After long standing a part of the oil crystallized. The crystals (0·55 g.) were pressed dry on a porous plate. They were insoluble in ether; but soluble in acetone, and had m. p. 91·5° after recrystallization from dioxan.

The project of which this work and that in the two following papers in part was sponsored in this Laboratory by Union Carbide Corporation, New York, N.Y. The author is grateful to Professor H. B. Henbest, Belfast, and Dr. B. Hargitay for stimulating discussions, and to Mr. M. Hubert for experimental assistance.

European Research Associates, 95, rue Gatti de Gamond, Brussels 18, Belgium. [*Received, July 4th*, 1960.]

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191. *The Stereochemistry of Polyborate Anions and of Borate Complexes of Diols and Certain Polyols.*

By Johannes Dale.

The possible monocyclic and condensed cyclic structures for the complex polyborate anions have been deduced from steric considerations. Among these, a possible tetrameric urotropine-like cage structure $[B_4O_6(OH)_4]^{4-}$ is suggested for the crystalline hydrates of sodium metaborate.

Monocyclic sodium borate complexes of several 1,2- and 1,3-diols, a spiran-type bisdiol monoborate complex of pinacol, a spiran-type bisborate complex of pentaerythritol, and tridentate cage complexes of 1,1,1-trishydroxymethylethane and *cis*-cyclohexane-1,3,5-triol, have been obtained crystalline from aqueous solution, and their structures proved by a study of thermal dehydration curves. The differences in stability between complexes and corresponding cyclic esters of the various types of diols and polyols are explained by stereochemical arguments.

cis- and *trans*-Cyclohexane-1,3-diol are readily separated by using the fact that the *cis*-isomer forms a distillable cyclic ester with boric acid, whereas the *trans*-isomer forms a polymer.

In the preceding paper the preferential formation of alkali borate complexes with one of the isomers in several sets of stereoisomeric 1,2- and 1,3-diols was reported and its use in the separation of such isomers was described without discussing in detail the structures of the complexes. Some of these complexes crystallized from water to give well-developed crystals which have now been investigated by chemical analysis, and, what is especially important from the structural point of view, by studying the dehydration curves recorded in a thermobalance to distinguish accurately between loosely bound water of crystallization and water bound structurally as hydroxyl groups on the boron atom. Simple stereochemical considerations led to an explanation of why 1,2-diols in general form more stable borate complexes than 1,3-diols, and to the prediction and subsequent isolation of stable cage structures, or tridentate complexes (which, however, had already been postulated by Mills, Angyal, and McHugh [1] from the ionophoretic behaviour of certain inositol isomers).

Before discussing these structures in detail we shall consider the structures of the

[1] Angyal and McHugh, *Chem. and Ind.*, **1956**, 1147; *J.*, 1957, 1423.

complex inorganic polyborate anions by a stereochemical analysis of boron compounds * similar to conformational analysis of cyclohexane derivatives.[2] There is some confusion about the structure of inorganic borates, not only in text-books, but even in recent publications,[3] in contrast to structural developments in borane and silicate chemistry. Also, it is now possible to check the results by recent accurate structure determinations of some borate minerals.[4–6]

To begin with, a few facts about the chemical behaviour of boric acid need be restated: (1) Boric acid behaves in aqueous solution exclusively as a monobasic acid;[7] hydrated salts with more than one cationic charge per boron atom are unknown. This means that boric acid acts, not as a proton donor, but as a Lewis acid, accepting the electron pair of the base (*e.g.*, OH^-) to form a tetrahedral anion.[7,8] (2) The weakness of boric acid is explained by its reluctance to sacrifice the mesomeric stabilization in its planar trigonal form (B–O distance [5] 1·37 Å) to assume the tetrahedral structure where no mesomerism is possible (B–O distance [5] 1·48 Å). (3) The low energy difference between structures with trigonal and tetrahedral boron and their ready interconversion explains the practically instantaneous establishment of equilibria in condensation and hydrolysis of boric acid and borates,[7,9] as well as in the formation and hydrolysis of boric acid esters.[10] (Of course, to complete an esterification, time may be required because water has sometimes to be removed from an equilibrium which, although reached instantaneously, may be unfavourable.) (4) In dilute solutions practically no polyions exist.[7]

Inorganic Polyborate Anions.—In condensations under dehydrating conditions the planar boric acid molecule has an obvious tendency to form a six-membered planar ring, α-metaboric acid [11] (I), not only because the OBO angle of 120° fits accurately, but also because the second valency from the oxygen has to form a 120° angle in the same plane to allow one electron pair in a π-orbital on the oxygen to overlap maximally with the vacant π-orbital on the boron atom. The ring thus becomes quasi-aromatic; and it may be noted that α-metaboric acid is isoelectronic with phloroglucinol.

The simple borate anion (III) with its tetrahedral OBO angle of 109·5°, which has been shown by *X*-ray analysis to be present in some double-salt minerals,[12,13] and by Raman spectroscopy to be the anion in solutions of sodium metaborate,[8] would fit well in a planar five-membered ring, which, however, is out of question because of the required boron–oxygen alternation. In the condensed six-membered ring (VI) which, as in the cyclohexane molecule, must be expected to assume the puckered chair conformation since there is no longer any mesomeric restriction on the oxygen atoms, the ring as such will be non-strained, but three of the six substituent hydroxyl groups must become axial and thereby cause a repulsive strain, which, however, can be relieved by condensing on another borate anion to form a urotropine- or adamantane-like cage structure (IX). This structure is probably present in the crystalline hydrates of sodium metaborate for the following reasons: (1) Infrared studies in progress in this laboratory show that the spectra are different from that of the simple ion (III) present [12,13] in teepleite, $NaB(OH)_4.NaCl$; the spectra are more complex and show resemblances with that of urotropine. (2) The

* [*Added in proof.*] A different approach to the structural analysis of polyborates has meanwhile been published by Edwards and Ross (*J. Inorg. Nuclear Chem.*, 1960, **15**, 329).

[2] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.
[3] *E.g.*, Carpéni, *Bull. Soc. chim. France*, 1949, **344**, 742; 1950, 1280.
[4] Morimoto, *Mineral. J. Japan*, 1956, **2**, 1.
[5] Christ, Clark, and Evans, *Acta Cryst.*, 1958, **11**, 761.
[6] Clark, *Acta Cryst.*, 1959, **12**, 162.
[7] Ingri, Lagerström, Frydman, and Sillén, *Acta Chem. Scand.*, 1957, **11**, 1034.
[8] Edwards, Morrison, Ross, and Schultz, *J. Amer. Chem. Soc.*, 1955, **77**, 266.
[9] Edwards, *J. Amer. Chem. Soc.*, 1953, **75**, 6151.
[10] Hermans, *Z. anorg. Chem.*, 1925, **142**, 83.
[11] Tazaki, *J. Sci. Hiroshima Univ.*, 1940, *A*, **10**, 55; *Struct. Rep.*, **8**, 211.
[12] Fornaseri, *Periodica Mineral. Rome*, 1949, **18**, 103; 1950, **19**, 157; *Struct. Rep.* **12**, 263.
[13] Collin, *Acta Cryst.*, 1951, **4**, 204.

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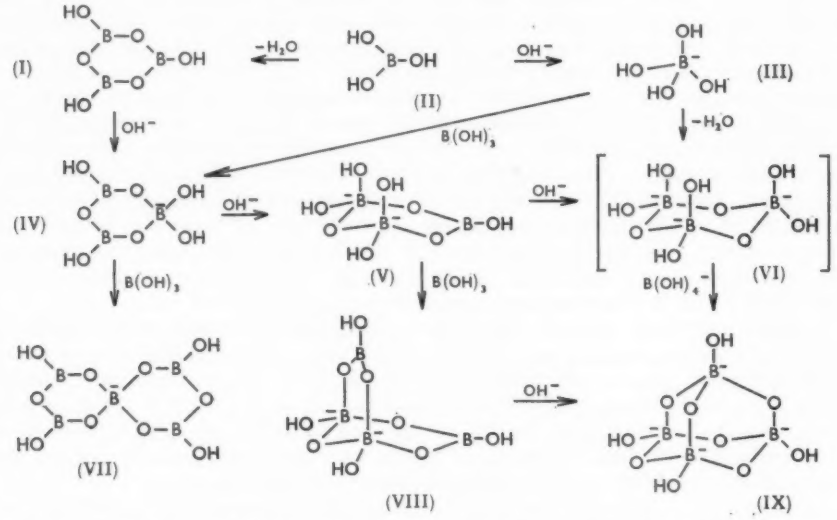
" tetrahydrate " of sodium metaborate loses water easily,[14] to form the " dihydrate " which on further dehydration [14,15] yields the " hemihydrate " whose tetrameric formula fits the cage structure (IX). (3) The unit cell of the " dihydrate " contains four boron atoms.[14]

Although none of these indications is proof of the cage structure, it is interesting that the last point at least definitely excludes the sterically unfavourable cyclic ion (VI), and that the corresponding " monohydrate " has never been observed.[14]



The annexed scheme also shows the structural relation between the various " mixed " polyborate anions. It is important that in all precisely determined crystal structures the number of tetrahedral boron atoms in a polyborate ion is equal to the number of cationic charges, the excess of boron atoms being trigonal planar. Starting from the α-metaboric acid (I), by neutralizing one boron atom the ion (IV), probably planar, is obtained. This may be the ion present in the so-called " triborate " of lithium [16] and has been considered from an analysis of titration curves to be the most important polyborate ion in sodium borate solutions.[7] By condensing on two more molecules of boric acid, the spiran structure (VII) is obtained, which, probably because of its higher symmetry, favours crystallisation, to give pentaborates, whose structure was established long ago by *X*-ray diffraction of the potassium salt.[17] Here again, the so-called " tetrahydrate " loses its two molecules of water of crystallization rather easily.[18] Also, nuclear magnetic resonance studies [19] confirm the presence of two molecules of water and four hydroxyl groups bound in the ion.*

When now the simple ring is doubly neutralized it has to be bent and the resultant dinegative ion (V) possesses some degree of instability because of its two axial hydroxyl

* [*Added in proof.*] Recently, the ion (IV) has been found to be the structural unit in the three-dimensional network of anhydrous cæsium triborate (Krogh-Moe, *Acta Cryst.*, 1960, **13**, 889), and the ion (VII) the basic unit in the network structure of anhydrous potassium and rubidium pentaborate (Krogh-Moe, *Arkiv Kemi*, 1959, **14**, 439).

[14] Menzel and Schulz, *Z. anorg. Chem.*, 1943, **251**, 167.
[15] Krc, *Analyt. Chem.*, 1951, **23**, 806.
[16] Filsinger, *Arch. Pharm.*, 1876, **208**, 211.
[17] Zachariasen, *Z. Krist.*, 1937, **98**, 266.
[18] Rosenheim and Leyser, *Z. anorg. Chem.*, 1921, **119**, 1.
[19] Smith and Richards, *Trans. Faraday Soc.*, 1952, **48**, 307.

groups. In spite of this, *X*-ray structural work has shown the dinegative ion (V) to be present in several borate minerals,[5,6] but, perhaps significantly, only combined with the dipositive calcium ion. The repulsive strain may be somewhat relieved by making the ring more planar (although thereby introducing ring strain), but the degree of departure from planarity cannot be read off with certainty from the published drawings of these structures. However, the strain in form (V) can be relieved completely by adding one molecule of boric acid to form the very stable tetraborate ion (VIII). It is therefore not surprising that it is this ion which is the most preponderant dinegative ion in sodium borate solutions,[20] and not the triborate ion (V) as proposed originally.[7] The structure of sodium tetraborate " decahydrate " (borax) has been determined [4] and found to contain the ion (VIII), and it is interesting that this salt, as well as the " pentahydrate," can be easily dehydrated to the " dihydrate " stage,[21] while further dehydration is slow and produces a glass. By neutralizing the two remaining boron atoms in (VIII), the two fused rings must assume the chair form, a sterically impossible situation except when an oxygen bridge is formed by loss of water to give again the cage structure (IX).

It should be emphasized that it is not possible for steric reasons to add further atoms or groups to form new condensed rings on the final polyborate structures (VII), (VIII), and (IX). Of course, the structural elements can be combined into chains linked by oxygen bridges, but this does not create any new stable, compact, and rigid elements. Thus, polymeric chains of the ring (V) are found in some calcium borate minerals [5] and, by combining different structural elements, possible structures can be suggested for the rare " octaborate " $Li_2B_8O_{13},6H_2O$,[16] and the unstable $K_2B_5O_9H,3H_2O$ [22] if the anions are written in the form $B_4O_4(OH)_5^-$ and $B_5O_5(OH)_7^{2-}$ respectively.*

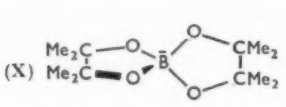
Borate Complexes of Diols and Polyols.—The striking steric similarity between the combination trico-ordinated boron–oxygen and olefinic or aromatic carbon on the one hand, and between tetraco-ordinated boron–oxygen and saturated carbon on the other hand, enables the stereochemistry of the diol–borate complexes to be considered in a completely analogous manner.

The sodium borate complexes of the 1,2- and 1,3-diols described in the preceding paper crystallized in general from water as simple 1 : 1 compounds with three molecules of water of crystallization. A precipitation of a crystalline spiran-type bisdiol monoborate complex was observed only in the case of pinacol, presumably because of the very high symmetry of this complex anion (X). The 1,3-diols must be expected to form borate complexes having six-membered non-planar cyclohexane-like ring systems. Proof of the puckered chair form with two types of substituent, axial and equatorial, was obtained from the observation that racemic pentane-2,4-diol with one axial methyl group forms a slightly less stable complex than the diequatorial *meso*-isomer, and that when the axial group is phenyl no complex is formed at all with the racemate. Further, 2,4-dimethylpentane-2,4-diol forms an ester with boric acid,[10] although it is somewhat unstable because of a single methyl–methyl axial interaction, but it gives no complex;[10] instead the ester is hydrolyzed when alkali is added, since there would have been three axial interactions in the complex (methyl–methyl and twice methyl–hydroxyl) (see XI and XII). Similarly, we have now found that *cis*-cyclohexane-1,3-diol forms a cyclic boric ester (XIII), but no complex (XIV) with sodium borate.

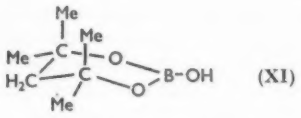
It should be mentioned that this ester (XIII) is formed less easily than those of other secondary 1,3-diols; thus, only the diol is extracted from an aqueous solution of the diol and boric acid. This can be understood if it is assumed that the *cis*-diol exists normally in the diequatorial conformation, at least in polar solvents, and has to become diaxial to react. The diequatorial conformation is indicated by *X*-ray data for the solid;[23] on

[20] Sillén, *Quart. Rev.*, 1959, **13**, 146.
[21] Menzel, Schulz, Sieg, and Vogt, *Z. anorg. Chem.*, 1935, **224**, 1.
[22] Carpéni, *Compt. rend.*, 1954, **239**, 1500.
[23] Furberg and Hassel, *Acta Chem. Scand.*, 1950, **4**, 597.

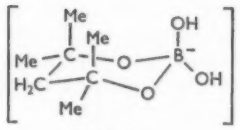
the other hand, the infrared spectrum [24] indicates an internally hydrogen-bonded diaxial conformation in dilute solution in carbon tetrachloride. *trans*-Cyclohexane-1,3-diol forms only a polymer with boric acid; therefore, by distilling off the cyclic ester of the *cis*-isomer, or rather a mixed ester with 1-hexanol (see p. 930), a mixture of the two isomers



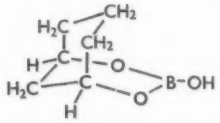
(X)



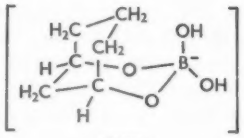
(XI)



(XII)



(XIII)



(XIV)

can be easily separated. This novel method is especially useful in this case, as the borate-complex method evidently cannot be used, and separation by fractional crystallization is extremely slow and tedious.[25]

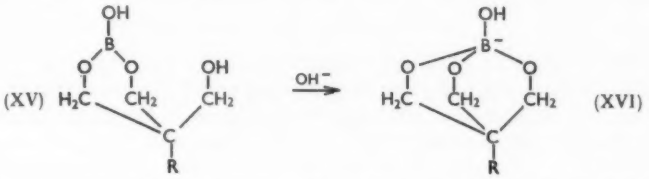
Several complexes of 1,2-diols have been prepared earlier by Hermans [10] and by Maan,[26] but, except for phenylethylene glycol,[10] they were all from cyclic diols. We have now isolated sodium borate complexes of the unsubstituted cyclic diols, *cis*-cyclopentane- and *cis*-cyclohexane-1,2-diol, and of the isomeric butane-2,3-diols. The essentially planar structure of the five-membered ring system is indicated by the fact that the cyclopentanediol forms a much stronger complex then the cyclohexanediol, and that the racemic butane-2,3-diol, with *trans*-disposition of the methyl groups, forms a much stronger complex than the *meso*-isomer with two methyl groups on the same side. It is also interesting that pinacol (2,3-dimethylbutane-2,3-diol) not only forms an ester,[10] but, as already mentioned, has now been found to form *also* a complex when alkali is added. This shows that there are no interacting groups as close as in the axial positions of the six-membered ring. Further indications of the planar structure are the existence of stable *cis*-cyclohexane- and *cis*-cyclopentane-1,2-diol complexes even with methyl substituents in the 1-position,[26] and the fact that only with the larger phenyl groups do the complexes become too unstable to be isolated.[26] If in the latter case the interaction with the hydroxyl group on the boron atom is removed by making boron trigonal, a stable ester would result, as in fact found with 1-phenylcyclopentane-1,2-diol.[26]

At first it seemed surprising that complexes with 1,2-diols were more stable than those with comparable 1,3-diols, when on the other hand the converse is true for the corresponding esters. Thus, secondary 1,2-diol esters deposit boric acid in water, whereas secondary 1,3-diol esters are usually formed directly by mixing the diol and boric acid together in water solution. However, if the structural requirements of the planar boric acid (or ester) system are considered, it is seen that to form a five-membered ring the angles, especially the BOC angles, have to be drastically reduced from the 120° required for maximal mesomeric interaction, thereby forcing the oxygen into sp^3-hybridization. When, therefore the tetrahedral anion is being formed, there is less mesomeric energy to lose and the strain can be completely removed. The possibility of forming, with tetrahedral boron, a ring structure which cannot be easily formed with trigonal boron, is therefore the driving force in the acidity increase of boric acid in the presence of 1,2-diols. In a six-membered ring both configurations of boron can be accommodated without strain; hence, there is no

[24] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.
[25] Rigby, *J.*, 1949, 1586.
[26] Maan, *Rec. Trav. chim.*, 1929, **48**, 332.

such strong driving force towards formation of a borate anion in the presence of 1,3-diols and the acidity of boric acid is not increased to a measurable extent.

The fact that pentaerythritol was the only compound, containing the 1,3-diol structure and no 1,2-diol structure, which was known to raise the acidity of boric acid to the same degree as 1,2-diols,[27] together with the fact that the dimethyl ether of pentaerythritol does not show this effect,[28] led us to the belief that a cage structure with three hydroxyl groups linked to the same boron atom might be involved. The driving force would then be found in the fact that the trigonal boron atom cannot link more than two of these hydroxyl groups, and only by becoming a tetrahedral anion would it be able to close the bridge to form the favourable cage structure (XV ⟶ XVI).*



This idea was supported by Brown and Fletcher's finding [29] that 1,1,1-trishydroxymethylpropane does not give a cage structure with boric acid, but only a polymer. We have now found that the same is true of 1,1,1-trishydroxymethylethane, even in the presence of organic bases, but also that this triol raises the acidity of boric acid to about the same degree as pentaerythritol and gives a crystalline complex with sodium borate. The analysis gives an empirical formula of $C_5H_{16}BNaO_7$, and the compound loses three mol. of water below 47° whereafter no further weight loss occurs below 230°. Since, in general, in the simple ring systems with two hydroxyl groups on the boron atom an additional mol. of water starts to come off at a slightly higher temperature than the water of crystallization, this shows that only one hydroxyl group remains on the boron atom, thus proving the cage structure.

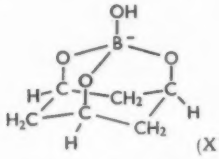
This cage structure can be considered as composed of three fused six-membered rings in the boat conformation, so an obvious extension was to make a complex with three fused rings in the chair conformation. α-Cyclohexane-1,3,5-triol (α-phloroglucitol), which has been shown by *X*-rays [30] to be the *cis*-isomer, was found to raise the acidity of boric acid to a similar degree and gave a crystalline complex with sodium borate. Again, above 48° (and below 300°) no further weight loss occurred, so that only one hydroxyl group remains on the boron atom, proving the urotropine-like cage structure (XVII). In contrast, the *trans*(β)-isomer gives no complex or increase in acidity. This incidentally furnishes, not only with a diagnostic tool for *cis*-cyclohexane-1,3,5-triol structures (cf. Angyal and McHugh [1]), as do other tridentate reactions to give, for example, phosphorous,[31] phosphoric,[31] thiophosphoric,[31] and orthocarboxylic esters,[32] but also provides a simple preparative method for separating such isomers. In the present case this is not of much use as the isomers are separable by crystallization,[33] but for non-crystalline derivatives the method should have potentialities.

* In complete formal analogy the observation that the acidity of boric acid increases with concentration, or, more exactly, that polyborates are salts of stronger acids than the simple boric acid,[7] may be explained by the fact that condensed structures can be formed with tetrahedral boron, which for steric reasons cannot be formed with trigonal boron. Thus, the acidity of boric acid is increased not only in the presence of diols and polyols, but also in the presence of boric acid itself.

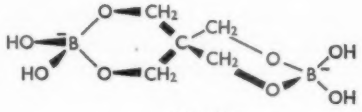
[27] Boëseken and Van Rossem, *Rec. Trav. chim.*, 1911, **30**, 392.
[28] Orthner and Freyss, *Annalen*, 1930, **484**, 131.
[29] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1951, **73**, 2808.
[30] Andersen and Hassel, *Acta Chem. Scand.*, 1948, **2**, 527; 1951, **5**, 1349.
[31] Stetter and Steinäcker, *Chem. Ber.*, 1952, **85**, 451.
[32] Stetter and Steinäcker, *Chem. Ber.*, 1953, **86**, 790; 1954, **87**, 205.
[33] Lindemann and Baumann, *Annalen*, 1930, **477**, 78.

XUM

When finally it was tried to isolate the complex of pentaerythritol, only an amorphous precipitate, probably a polymer, was obtained from a very concentrated solution when equimolar quantities were used. When a large excess of sodium borate was used, a crystalline complex was obtained which, however, proved to be of the bis-type having the spiran structure (XVIII). Apparently, the free hydroxyl group in the tridentate complex,



(XVII)



(XVIII)

which undoubtedly must be the main species in solution, renders it too soluble, so that other less soluble species, even when present as minor constituents, may crystallize instead. Caution is therefore needed when drawing conclusions as to the composition of a borate solution from the substances precipitated.

Experimental

Preparation and Analysis of Sodium Borate Complexes.—The sodium borate complexes were, except when otherwise stated, prepared by heating equimolar quantities of the diol (or polyol) and sodium metaborate in water containing a little extra sodium hydroxide to prevent precipitation of borax. After cooling, the crystals were filtered off and wiped on filter paper. When the complexes crystallized as very thin leaflets, this method was not very efficient, as shown by unsatisfactory analyses. The complexes were analyzed by potentiometric titration, first with hydrochloric acid to determine sodium, then with sodium hydroxide in the presence of mannitol to determine boron. Ordinary combustion analysis was used to obtain the values for carbon and hydrogen. Finally, the dehydration curve in air of samples of about 100 mg. was recorded on a Stanton thermobalance modified to obtain a rate of temperature rise as slow as to require about 6 hr. to reach 200°. Usually, the transparent crystals became white and opaque when the water of crystallization was lost, but did not melt below 330°. The dehydration was completely reversible at least up to about 120°, so that the dried sample picked up exactly the lost quantity of water when exposed to the atmosphere.

meso-*Pentane*-2,4-*diol*.—The *complex* crystallized as thin flakes (Found: C, 26·55; H, 8·15; B, 4·7; Na, 10·15. $C_5H_{18}BNaO_7$ requires C, 26·8; H, 8·1; B, 4·8; Na, 10·3%). Between 50° and 105° it lost rapidly 24·0% of its weight ($3H_2O$ requires 24·1%); up to 150° there was a less rapid loss of about 8% ($1H_2O$ requires 8·0%); and above 150° the weight loss continued at a still somewhat slower rate. The dried complex (100°) was insoluble in ether, chloroform, benzene, or tetrahydrofuran, but soluble in hot xylene or pyridine, apparently with dehydration to give polymers since gels were formed on cooling.

Racemic Pentane-2,4-*diol*.—The *complex* was obtained as irregularly shaped crystals (Found: C, 26·3; H, 8·3; B, 4·7; Na, 10·2%). Between 50° and 100° it lost rapidly 24·1% of its weight; up to 140° the loss was less rapid and amounted to about 8·5%; it then continued at a still slower rate at higher temperatures.

meso-*Butane*-2,3-*diol*.—The *complex* crystallized from relatively concentrated solutions as thin flakes (Found: C, 23·15; H, 7·8; B, 5·0; Na, 10·7. $C_4H_{16}BNaO_7$ requires C, 22·9; H, 7·7; B, 5·15; Na, 10·95%). It lost rapidly 25·6% of its weight ($3H_2O$ require 25·7%) between 55° and 95°; above this temperature a much slower loss continued without stop.

Racemic Butane-2,3-*diol*.—The *complex* crystallized as thick oblong hexagonal plates (Found: C, 23·0; H, 7·9; B, 5·2; Na, 10·9%). Between 70° and 130° it lost rapidly 25·8% of its weight, with little further loss to 145°, above which temperature the loss continued slowly with no stop.

cis-*Cyclopentane*-1,2-*diol*.—The *complex* crystallized as irregular plates (Found: C, 26·95; H, 7·5; B, 5·05; Na, 10·2. $C_5H_{16}BNaO_7$ requires C, 27·05; H, 7·3; B, 4·9; Na, 10·35%). Between 50° and 90° it lost rapidly 24·3% of its weight ($3H_2O$ require 24·4%), with little further loss to 125°, whereafter slow loss continued without stop.

cis-*Cyclohexane*-1,2-*diol*.—The *complex* was obtained from concentrated solutions as very

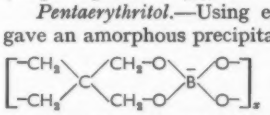
thin shiny flakes (Found: C, 29·9; H, 7·8; B, 4·6; Na, 9·7. $C_6H_{18}BNaO_7$ requires C, 30·5; H, 7·7; B, 4·6; Na, 9·75%). It lost rapidly 21·6% of its weight between 53° and 90° ($3H_2O$ require 22·9%). Above 90° a slow loss continued without stop.

Pinacol.—A complex was precipitated very slowly on mixing equimolar quantities of pinacol and sodium borate. It proved to be the bisdiol borate, and was later found to crystallize more easily when twice as much pinacol was used. The very concentrated solution had to be filtered hot to remove some oil droplets (pinacolone?), and on cooling, the 2 : 1 *complex* crystallized as large, but extremely thin, leaflets which broke easily to give a powder. It contained four mol. of water of crystallization (Found: C, 43·1; H, 9·8; B, 3·2; Na, 7·0. $C_{12}H_{32}BNaO_8$ requires C, 42·6; H, 9·55; B, 3·2; Na, 6·8%). Between 40° and 80° it lost rapidly 20·9% of its weight ($4H_2O$ require 21·3%), but no more up to 170°. Above 170° a slow loss started. Titration of the complex with hydrochloric acid had to be carried out slowly as the hydrolysis was very slow compared with that of the other simple complexes.

1,1,1-*Trishydroxymethylethane.*—The *complex* crystallized as very long flakes which broke easily (Found: C, 27·1; H, 7·35; B, 5·0; Na, 10·3. $C_5H_{16}BNaO_7$ requires C, 27·05; H, 7·25; B, 4·9; Na, 10·35%). It lost rapidly 24·0% of its weight between 35° and 47° ($3H_2O$ require 24·4%), then no more up to 230°. Above this temperature a rapid loss started.

α-*Cyclohexane*-1,3,5-*triol.*—The *complex* of the α-(*cis*-)isomer (for the preparation see below) crystallized as oblong flakes (Found: C, 30·8; H, 7·1; B, 4·7; Na, 9·65. $C_6H_{16}BNaO_7$ requires C, 30·8; H, 6·9; B, 4·6; Na, 9·8%). Between 35° and 48° it lost rapidly 22·8% of its weight ($3H_2O$ require 23·1%), then no more up to 300°, whereafter rapid weight loss occurred.

Pentaerythritol.—Using equimolar quantities of pentaerythritol and sodium metaborate, gave an amorphous precipitate from concentrated solutions. This was filtered off and pressed between filter paper, but had to be dried in air at 20° to reach a constant weight. Analysis showed it to be a 1 : 1 *complex*, probably polymeric (see inset) containing six mol. of water of crystallization (Found: C, 20·9; H, 7·8; B, 4·05; Na, 8·2. $C_5H_{20}BNaO_{10}$ requires C, 21·9; H, 7·4; B, 3·95; Na, 8·4%). It lost rapidly 39·2% of its weight between 30° and 80° ($6H_2O$ require 39·5%), whereafter a slow loss continued without stop.



When substantially more than two moles of sodium borate were used per mole of pentaerythritol, thin needles crystallized already from much more dilute solutions. Analysis showed it to be the *diborate* (*i.e.*, the 1 : 2 complex) containing twelve mol. of water of crystallization (Found: C, 12·6; H, 7·55; B, 4·4; Na, 9·45. $C_5H_{36}B_2Na_2O_{20}$ requires C, 12·4; H, 7·45; B, 4·45; Na, 9·5%). If heated quickly, the crystals melt above 75°, then solidify again as the water evaporates. If they are heated slowly, no melting occurs below 350°. On the thermobalance the complex lost rapidly 36·4% of its weight between 40° and 65° ($10H_2O$ require 37·1%); between 65° and 95° it lost more slowly 7·4% ($2H_2O$ require 7·4%); and above 95° a still slower loss continued without stop.

The infrared spectra of the two complexes are very similar, and different from that of the borate complex of 1,1,1-trishydroxymethylethane; hence, a tridentate cage structure is excluded.

Attempts to prepare Borate Complexes of 1,1,1-*Trishydroxymethylethane in the Presence of Amines.*—(a) *Tributylamine.* Molar quantities of the triol, boric acid, and tributylamine were heated together, rapidly becoming homogeneous. In less than 1 hr. the theoretical amount of water had distilled off. After cooling, a solid mass was deposited. The supernatant liquid (pure tributylamine) was decanted. The solid was non-volatile, burned with a green flame, and must be a polymeric triol borate. When heated it fused, giving a hard brittle glass, soluble with decomposition in water and acids.

(b) *Pyrrolidine.* When the much stronger base pyrrolidine was used and the water removed by azeotropic distillation with chloroform, the expected quantity of a homogeneous yellow solid was obtained after removal of the solvent *in vacuo*. It was tough when hot, and brittle when cold, soluble in water (with decomp.) and chloroform, but insoluble in benzene, and burned with a green flame. Surprisingly, attempts to sublime or distil the expected compound $Me{\cdot}C(CH_2{\cdot}O^-)_3B \leftarrow HNC_4H_8$ only led to decomposition of the solid, so either the B ← N link is thermally unstable, or the base is linked differently to a triol borate polymer instead of to the tridentate complex.

Preparation of Cyclohexane-1,3,5-*triol* (*Phloroglucitol*).—Phloroglucinol (100 g.) in absolute ethanol (100 ml.) containing Raney nickel (15 g.) and sodium hydroxide (0·5 g.) was hydrogenated at a constant pressure of 140—150 atm. The uptake started at 90° and was essentially complete

at 125° in 30 min. The products were worked up and the isomers separated as described by Lindemann and Baumann.[33] The yield of the *cis*-isomer (α-phloroglucitol; m. p. 185°) was 26%, and of the *trans*-isomer (β-phloroglucitol; m. p. 145°) 20%. Yields of 60% of α and 10% of β have been reported [31] for a similar hydrogenation carried out at 50°/1 atm.

When it was tried to prepare a sodium borate complex of the *trans*-isomer, very pure unchanged triol crystallized on cooling.

Separation of cis- *and* trans-*Cyclohexane*-1,3-*diol*.—The crude cyclohexane-1,3-diol was prepared by catalytic hydrogenation of resorcinol under the conditions reported by Clarke and Owen,[34] but with Raney nickel furnished by Fluka AG. The reaction was much faster and complete in 30 min., and the quantity of cyclohexanol formed was negligible. The diol distilled at 118—122°/7 mm. (yield 71%; n_D^{20} 1·4980). The liquid diol mixture (58 g.) was heated with trihexyl borate (204 g.), and the liberated hexan-1-ol (86 g.) distilled off at 153°. On further distillation, *in vacuo*, the mixed ester, *cis*-cyclohexane-1,3-diol hexyl borate (83·1 g.), n_D^{21} 1·4390, passed over at 107—120°/0·8 mm. Then the temperature started to rise and the index of refraction dropped to 1·4275 (trihexyl borate has n_D^{21} 1·4260). At the same time the polymeric borate of the *trans*-diol started to separate.

cis-Cyclohexane-1,3-diol was isolated by dissolving the distilled mixed ester in concentrated alkali, extracting the solution with ether (no sodium borate complex was formed), and distilling the extract. Hexan-1-ol distilled first, then the *cis*-diol (40 g., 70%) at 100—104°/0·5 mm. After recrystallization from acetone the diol melted at 82—83°.

The *trans*-cyclohexane-1,3-diol was isolated similarly from the residue, which contained some trihexyl borate. The *trans*-diol (15·6 g., 27%) distilled at 130—142°/6 mm. and, recrystallized from acetone, had m. p. 118—120°.

Separation is also possible if the hexanol is replaced by pentanol, but it is more difficult to get a clear separation by distillation of the mixed ester and the excess of tripentyl borate. This is necessary, as the last portion of the liquid is hard to remove completely from the polymer and therefore should not contain the *cis*-isomer.

cis-*Cyclohexane*-1,3-*diol Borate*.—When a solution of the *cis*-diol and boric acid in water was extracted with ether, no borate was obtained but only the pure diol. Similarly, an attempt at partial hydrolysis of *cis*-cyclohexane-1,3-diol hexyl borate by the addition of one mol. of water failed to yield the simple cyclic ester; instead, boric acid was precipitated.

A mixture of *cis*-cyclohexane-1,3-diol and boric acid was then heated in benzene and the water formed was removed azeotropically. When the calculated quantity of water had been collected, the excess of boric acid was filtered off, the solution concentrated, and hexane added. A mixture of a powder and needles was obtained. The rest was evaporated, and sublimed with difficulty *in vacuo*. This sublimate was also heterogeneous and was recrystallized from hexane, giving long thin needles of the *diol borate*, m. p. 165—180° when determined slowly (Found: B, 7·5; $C_6H_{11}BO_3$ requires B, 7·6%). On a Kofler bank it first melted at 105—110°, then solidified and remelted at 180° as the *anhydride* (Found: B, 8·4. $C_{12}H_{20}B_2O_5$ requires B, 8·2%).

When the borate was treated with alkali, no precipitate was formed but the diol separated as an oil.

The author is grateful to Dr. B. Hargitay for valuable suggestions and discussions, and to Mr. M. Hubert for experimental assistance.

European Research Associates, 95, rue Gatti de Gamond, Brussels, Belgium. [*Received, July 4th*, 1960.]

[34] Clarke and Owen, *J.*, 1950, 2103.

192. *The Structure and Relative Stabilities of Boric Esters of 1,2- and 1,3-Diols.*

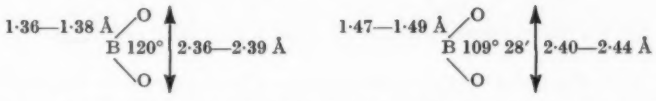
By A. J. Hubert, B. Hargitay, and Johannes Dale.

Cyclic boric esters of 1,2-diols show a much greater heat of reaction with amines than do cyclic esters of 1,3-diols and non-cyclic borates.

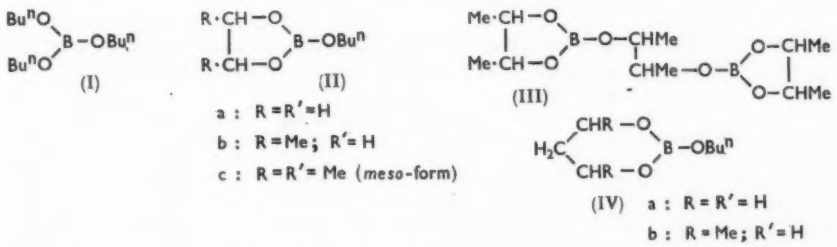
Isolation of the acetylation products of the mixed ester resulting from a competitive reaction between ethylene glycol and propane-1,3-diol for boric acid shows that the cyclic ester of the 1,3-diol is formed preferentially.

It is concluded that the five-membered ring must be strained with trigonal boron but not with tetrahedral boron, whereas the six-membered ring is unstrained in both cases. The strain in the five-membered ring approximately offsets the energy gain in ring formation, so that 1,2-diol borates, although distillable as cyclic esters, rearrange more or less to open-chain polymers on condensation. The unstrained 1,3-diol borates remain in the cyclic form.

From the work of Böeseken and his collaborators [1] it is known that many 1,2- but not 1,3-diols raise the acidity and conductivity of boric acid by complex formation. On the other hand, Hermans,[2] and later other workers,[3] have shown that boric esters are formed more readily from 1,3- than from 1,2-diols. In an early stereochemical treatment Hermans [4]



suggested that the difference in stability is caused by the different O–O distances for trigonal (2·32 Å) and tetrahedral boron (2·42 Å), the first of which fits better with 1,3-diols, the latter better with 1,2-diols. Newer results [5] show that the two O–O distances are really much closer and the difference probably too small to account for such a strong effect.



In the preceding paper it was shown that 1,3-diols also give stable complexes in alkaline solution, and a more modern stereochemical analysis was given which indicated that the angular requirements of the mesomerically stabilized planar boric acid system [6] (BOC angle 120°) must be mainly responsible for the strain in the five-membered ring. This strain can be relieved by forming the borate anion whereby, not only the boron atom, but also the oxygen atoms become " tetrahedral." In the non-planar six-membered ring no strain would be expected with either trigonal or tetrahedral boron.

[1] Böeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189.
[2] Hermans, *Z. anorg. Chem.*, 1925, **142**, 83.
[3] Pastureau and Veiler, *Compt. rend.*, 1936, **202**, 1683.
[4] Hermans, *Rec. Trav. chim.*, 1938, **57**, 333.
[5] Christ, Clark, and Evans, *Acta Cryst.*, 1958, **11**, 761.
[6] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 1529.

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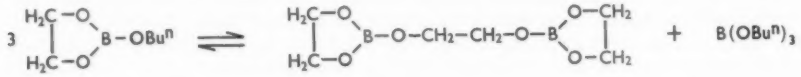
The expected great difference in the base-accepting power of five- and six-membered cyclic borates has now been confirmed by calorimetric measurements of the reaction with organic bases. These bases have a suitable base strength, allowing comparison, and permit work in hydroxyl-free solvents, whereby complicating solvolyses are avoided.

The borates used were of the simplest possible type, namely, (I—IV), to avoid steric effects by ring substituents. Qualitative comparison of the behaviour of these esters towards benzylamine showed that only compounds (II and III) containing the five-membered ring system gave a noticeable heat effect and a precipitate. The precipitates were too unstable to be recrystallized without decomposition. The amine and the borate contents, determined by titration (see Table 1), demonstrate that they are 1 : 1 addition



compounds, although the values obtained for the mixed esters (IIa and c) are appreciably lower than the calculated values. Probably the mixed esters are in part disproportionated [7] in the liquid phase into tributyl borate and the trisdiol diborate, as shown. A part of the precipitate would then consist of the addition product of the trisdiol diborate with a lower equivalent weight (the tributyl borate gives no precipitate). This explanation is supported by the correct and even too high values obtained with tri(butane-2,3-diol) diborate (III) in which such a disproportionation cannot take place.

After the nature of the reaction had been established as addition of the amine to the boron atom, and not for example an aminolysis [8] with liberation of butanol, the heat effect

TABLE 1. *Equivalent weight of precipitates of boric esters with benzylamine.*

Borate	Titr. HCl	Titr. NaOH	Theor.
Ethylene glycol butyl (IIa)	230	225	250
* *meso*-Butane-2,3-diol butyl (IIc)	268	263	274
meso-Butane-2,3-diol (III)	262	250	250

* Commercial butane-2,3-diol (Fluka) shown by us to contain 98·5% of *meso*-diol and 1·5% of racemate.

TABLE 2. *Thermal effect in the reaction between boric esters and amines in octane (12·5 mmoles of borate + 12·5 mmoles of amine in 96 ml. of octane).*

	Benzylamine		Pyrrolidine	
Borate	Obs. ΔH^1 (cal./mole)	$\Delta H = \Delta H^1 - \Delta H_{dil}$ [a]	Obs. ΔH^1 (cal./mole)	$\Delta H = \Delta H^1 - \Delta H_{dil}$ [b]
Tributyl (I)	+1130	−750	+770	−480
Ethylene glycol butyl (IIa)	−7750 [c]	−9630	−7100	−8350
Propane-1,2-diol butyl (IIb)	−2800 [d]	−4680	−9300	−10,550
meso-Butane-2,3-diol butyl (IIc) ...	−1580 [c]	−3460	−7100	−8350
meso-Butane-2,3-diol (III)	[c]		−8700	−9950
Propane-1,3-diol butyl (IVa)	+1400	−480	−650	−1900
Butane-1,3-diol butyl (IVb)	+1280	−600	+770	−480

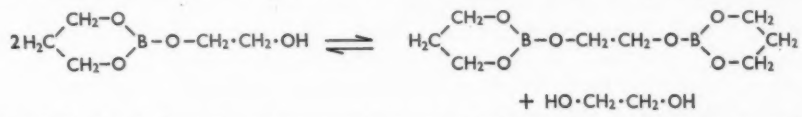
[a] $\Delta H_{dilution}$ = 1800 cal./mole. [b] $\Delta H_{dilution}$ = 1250 cal./mole. [c] Solid precipitate. [d] Gelatinous precipitate.

was determined calorimetrically for octane solution with benzylamine and the stronger base pyrrolidine. The latter base did not give a precipitate with any of the borates, which was an advantage; the medium being homogeneous throughout the measurement, the heat of crystallization of the product did not obscure the effect. The heat of dilution of the concentrated amine in octane, separately measured, had to be subtracted from the observed heats of reaction. The results are given in Table 2.

[7] Thomas, *J.*, 1946, 823.
[8] Goubeau *et al.*, *Z. anorg. Chem.*, 1951, **266**, 161; 1951, **267**, 27; 1952, **268**, 145.

It will be noticed that, although pyrrolidine is a stronger base than benzylamine, the borate (IIa) shows a higher apparent heat of reaction with benzylamine. This is presumably due to the additional heat of crystallization, since this complex is much less soluble than the other benzylamine complexes (with methyl substituents) and is precipitated more completely. On this basis the results obtained with pyrrolidine are more reliable, and it is seen that cyclic 1,2-diol borates are throughout far more acidic than cyclic 1,3-diol borates and open-chain borates.

To determine the relative stabilities of the boric esters as such, a mixture of one mol. of ethylene glycol and one of propane-1,3-diol was esterified with one mol. of boric acid. If now, as expected, the 1,3-diol forms preferentially the cyclic ester, a mixed ester, which might possibly in part be disproportionated into the trisdiol diborate and free ethylene glycol, should be formed. It was in fact found that, after the free hydroxyl groups had been caused to react with acetyl chloride, it was possible after mild hydrolysis to isolate as



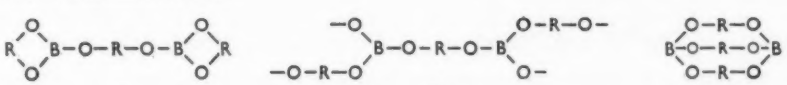
+ HO·CH$_2$·CH$_2$·OH

main products ethylene glycol monoacetate and ethylene chlorohydrin acetate, and only very little of the corresponding propanediol derivatives (Table 3). Acetyl chloride was chosen as reagent because neither it nor the hydrogen chloride formed attacks boric esters, and because the reaction was rapid and the products were easily separated by distillation. An analogous procedure has been used in a structural study of methyl D-glucopyranoside:[9] its boric ester was treated with benzoyl chloride and the benzoylated products were identified after hydrolysis.

TABLE 3. *Acetylation of mixed boric esters of diols.*

Product treated with AcCl (0·5 mol.)	Isolated products (in moles)						Recovery (%)
	OH [CH$_2$]$_2$ Cl	OAc [CH$_2$]$_2$ Cl	OAc [CH$_2$]$_2$ OH	OH [CH$_2$]$_3$ Cl	OAc [CH$_2$]$_3$ Cl	OAc [CH$_2$]$_3$ OH	
Ester between ethylene glycol (1 mol.) and boric acid (0·5 mol.)	0·02	0·21	0·11				68
Ester between propane-1,3-diol (1 mol.) and boric acid (0·5 mol.) ...				0·03	0·02	0·24	58
Mixed ester between ethylene glycol (0·5 mol.), propane-1,3-diol (0·5 mol.), and boric acid (0·5 mol.) ...	0·01	0·17	0·19		0·01	0·04	84
Mixture of free ethylene glycol (0·5 mol.) and propanediol (0·5 mol.)...	0·10	0·04	0·04	0·01	0·01	0·24	88

To make sure that the ethylene glycol derivatives were not formed by a secondary exchange, a mixture of the two free diols was treated with acetyl chloride sufficient for only one partner: propanediol monoacetate was the main product. As a further check on the method and as an aid in the identification of the products, the borates of each of the diols alone were tested. The results are included in Table 3, and it is evident from the results of the competitive reaction that boric acid forms the six-membered ring much more easily than the five-membered one.



(A) (B) (C)

The main reason for the greater heat effect with amines is clearly that the strain in the five-membered ring can be relieved by converting the planar trigonal into the tetrahedral

[9] Sugihara and Petersen, *J. Amer. Chem. Soc.*, 1956, **78**, 1760.

boron atom. The strain seems approximately to cancel the energy gain on cyclization, as can be seen from the fact that whereas tris-(1,3-diol) diborates remain liquid indefinitely, and therefore are assigned the structure (A), the corresponding 1,2-diol borates, although distillable, become very viscous or even glassy after condensation (cf. Thomas [7]). The structure (A) must therefore in this case be in equilibrium with open-chain polymer structures such as (B).

Several of these esters have been prepared (see Table 4). The contribution of the polymer structure seems to diminish with increasing substitution, presumably because of increasing steric difficulties brought about by the methyl groups in the network structure. A similar trend is observed in the cryoscopic molecular-weight determinations of ethyleneglycol butyl borate (IIa) and the tri(propane-1,2-diol) diborate. The former has a much too high molecular weight in concentrated benzene solution which drops off towards the normal value on dilution, whereas with the latter a constant normal value is obtained even at higher concentrations (Table 5). Similarly, a comparison of the heats of dilution in octane shows that the five-membered ring structure (IIa) with a value of 2200 cal./mole must be more " associated " in the liquid state than in dilute solution. The value 1130 cal./mole obtained with the six-membered ring structure (IVa) indicates a smaller structural change on dilution.

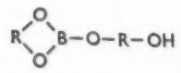
TABLE 4. *Trisdiol diborates.*

Diol	Equivalent weight Theor.	Found	
HO·CH_2·CH_2·OH	101	103	Glass
HO·CHMe·CH_2·OH	122	125	Gelatinous liquid
HO·CHMe·CHMe·OH (*meso*)	143	143	Very viscous liquid
HO·CH_2·CH_2·CH_2·OH	122	121	Liquid

TABLE 5. *Molecular-weight determinations by cryoscopy in benzene.*

(IIa):	Concn. (g./100 ml.)	4·17	2·77	2·08	1·39	1·04	0 (extrap.)	Theor.
	M	208	198	188	176	171	154	144
(–O·CHMe·CH_2·O–)$_3B_2$:	Concn. (g./100 ml.)	6·75	4·50	3·38			0 (extrap.)	Theor.
	M	254	253	255			254	244

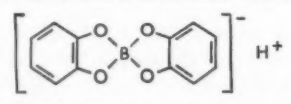
The ease with which boric acid esters form and rearrange explains why predominantly polymeric esters can be distilled completely in the form of their most volatile structure, with continuous displacement of the equilibrium.

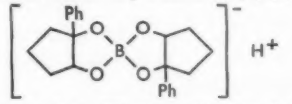


The observation was also made that bisdiol borates, although they can sometimes be isolated by crystallization,* cannot be distilled as such, but disproportionate, whereby the diol distils first, and the trisdiol diborate (A) afterwards. The only mixed esters which can be distilled are of the diol alkyl type (II and IV) in which the alcohol must be of such a size that the mixed ester is more volatile than the trialkyl borate.

The triply-bridged cage structure (C) proposed by Dupire [13] seems impossible for steric reasons for 1,2- and 1,3-diols, and improbable even for 1,4-diols, since molecular models

* The compounds assigned the annexed " acid " structures by Meulenhoff [10] and by Maan [11] are probably simple bisdiol borates in as much as the open structure of a crystalline bis-(2,2,5,5-tetramethyl-





hexane-3,4-diol) borate has been proved by the presence of an OH absorption band in the infrared spectrum.[12]

[10] Meulenhoff, *Z. anorg. Chem.*, 1925, **142**, 373.
[11] Maan, *Rec. Trav. chim.*, 1929, **48**, 332.
[12] Dale, preceding papers.
[13] Dupire, *Compt. rend.*, 1936, **202**, 2086.

show that the structure (A) with seven-membered rings and the structure (B) are much less strained. Several attempts to distil tri(butane-1,4-diol) diborate were unsuccessful, indicating that in this case the structure is completely polymeric (B). However, substituted 1,4-diols may well be more difficult to accommodate sterically in structure (B), and definitely in structure (C). The distillable tris-(2,5-dimethylhexane-2,5-diol) diborate which was obtained by Steinberg and Hunter [14] and for which the cage structure was proposed, has therefore probably the structure (A). This is supported by the finding that seven-membered cyclic benzeneboronates are stable and even preferred structures in certain cases.[15]

Experimental

Tributyl Borate (I).—The ester was prepared from butan-1-ol and boric acid by azeotropic distillation of the water with excess of butan-1-ol [16] and purified by vacuum-distillation.

Diol Butyl Borates (II *and* IV).—The mixed esters were prepared by the method used by Letsinger and Skoog [17] for the preparation of ethylene glycol butyl borate. Equimolar quantities of diol and tributyl borate were mixed; the butanol formed by alcoholysis of the tributyl borate was distilled off through a Vigreux column, and the mixed ester finally distilled at reduced pressure. Data for the products are given in Table 6. The equivalent weights were determined by potentiometric titration with sodium hydroxide in the presence of mannitol.

Attempts to prepare the analogous ester with butane-1,4-diol led only to a polymer.

Bisdiol Borates.—A mixture of 2 mol. of ethylene glycol or propane-1,3-diol and 1 mol. of boric acid was heated in chloroform, and the calculated quantity of water removed by azeotropic distillation. After evaporation of the chloroform a viscous residue was obtained (cf. Blau, Gerrard, and Lappert [18]) which was soluble in chloroform and benzene. When distilled, disproportionation took place, as the diol and then the trisdiol diborate were obtained, neither of which was soluble in chloroform or benzene in the case of ethylene glycol.

Trisdiol Diborates.—These esters were obtained by esterification of 2 mol. of boric acid with 3 mol. of diol.[13,19,20] The water was removed by azeotropic distillation with chloroform or benzene. The esters were distilled at reduced pressure. The infrared spectra showed the absence of hydroxyl groups. Data for the products are given in Table 4.

Table 6. *Diol butyl borates*

R	B. p./mm.	Equivalent weight Theor.	Found	
·CH_2·CH_2·	97°/11	144	147	Viscous liquid
·CHMe·CH_2·	98°/11	158	153	Liquid
·CHMe·CHMe·	92°/13	172	173	Liquid
·CH_2·CH_2·CH_2·	98°/12	158	164	Liquid
·CHMe·CH_2·CH_2·	101°/13	172	178	Liquid

Isolation of Addition Compounds of Benzylamine with Boric Esters.—When a solution of a 1,2-diol borate in pentane or hexane was mixed with one of benzylamine in the same solvent, a precipitate was formed. This was unstable and had to be filtered off quickly,[7] washed with pentane, then dried for 15 min. in an oil-pump vacuum. Attempts to recrystallize the substances resulted in decomposition. The amine content was determined by titration with 0·1N-hydrochloric acid; then mannitol was added and the boron content determined by back-titration with 0·1N-sodium hydroxide (Table 1).

When ethylene glycol butyl borate (IIa) was treated with dry ammonia, a solid was obtained which rapidly liquefied (decomposition) *in vacuo* or if heated at ordinary pressure.

Calorimetric Measurements.—A very simple calorimeter consisting of a 250 ml. Dewar flask,

[14] Steinberg and Hunter, *Ind. Eng. Chem.*, 1957, **49**, 174.
[15] Sugihara and Bowman, *J. Amer. Chem. Soc.*, 1958, **80**, 2443.
[16] *Org. Synth.*, 1957, Coll. Vol. II, p. 106.
[17] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174.
[18] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.
[19] Morell and Lathrop, *J. Amer. Chem. Soc.*, 1945, **67**, 879.
[20] Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5497.

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a Beckmann thermometer, a known resistance, and a stirrer, was used. The resistance was used for the calibration by passing a current through it for a short period. The reproducibility was ±5%.

Octane (96 ml.) containing the boric ester (12·5 mmoles) was introduced into the Dewar flask. Then a very thin-walled sealed glass phial containing the amine (12·5 mmoles) and octane (1 ml.) was immersed in the solution and thermal equilibrium established during 30 min. while stirring. The phial was then broken with the stirrer and the temperature variation with time followed. After a very sharp rise (or fall) the temperature became fairly constant and diminished (or increased) by only 0·01—0·02°/min. Identical measurements with the amine in the absence of borate allowed a correction for the heat of dilution of the amine in octane to be applied. The results are given in Table 2.

In the same way the heat of dissolution, or dilution, of some boric esters (12·5 mmoles) in octane (100 ml.) was determined. The value obtained for ethylene glycol butyl borate (IIa) was +2200 cal./mole; for propane-1,3-diol butyl borate (IVa) it was +1130 cal./mole.

Molecular-weight Determinations.—Cryoscopic measurements were carried out in a classical Beckmann apparatus with benzene as a solvent and naphthalene for the calibration. The results are given in Table 5.

Acetylation of Bisdiol Borates.—0·5 Mol. of boric acid was esterified with a total of 1·0 mol. of diol by azeotropic distillation of the water with chloroform. When 1·5 mol. of water had been collected, the solution had become homogeneous and was left to cool to room temperature. 0·5 mol. of acetyl chloride in chloroform was slowly added. Hydrogen chloride was evolved and the solution became warm. After complete addition, the solution was refluxed for 5 min., then cooled and washed with sodium hydrogen carbonate, and the chloroform was evaporated. The residue was fractionally distilled on a spinning band column at reduced pressure. Elemental analysis, infrared spectrum, and b. p. determination at atmospheric pressure were used for the identification of each fraction. In a first experiment ethylene glycol was used alone to facilitate the identification of the acetylated products, then propane-1,3-diol alone, and finally the mixture of both. The results are presented in Table 3 together with the results of an acetylation experiment on an equimolar mixture of the diols in the absence of boroic acid and with acetyl chloride sufficient for only one partner.

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[*Received, July 4th*, 1960.]

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193. *Potential Anti-tumour Agents. Part I. Polyporic Acid Series.*

By B. F. CAIN.

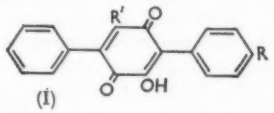
A series of compounds related to polyporic acid has been prepared for evaluation of their tumour-damaging capacity. Modifications not possessing the central 2,5-dihydroxyquinone nucleus have no anti-tumour activity.

EARLY in 1955 a screening programme was initiated for examining the indigenous New Zealand flora for anti-tumour agents. The first reproducible and significant results were obtained with a crude extract from the lichen *Sticta coronata* Mull Arg., whose biological activity, as indicated in a preliminary communication,[1] is due to the presence of polyporic acid (I; R = H, R′ = OH). The occurrence of this acid in *Sticta* species had been demonstrated previously by Murray,[2] but no prior reference to its anti-tumour effectiveness has been found although its anti-bacterial properties have been listed.[3]

In common with similar materials, to be described later, polyporic acid separates from large volumes of toluene in bronze plates of marked metallic appearance. However,

[1] Burton and Cain, *Nature*, 1959, **184**, 1326.
[2] Murray, *J.*, 1952, 1345.
[3] Akagi, Hirose, Watanabe, and Ose, *Ann. Proc. Gifu Coll. Pharm.* No. 4, 1954, **35**; *Chem. Abs.*, 1956, **50**, 14,865.

crystallization from dioxan or pyridine yields yellow or red solvates, respectively. The pyridine complexes should not be confused with the pyridinium salts. The anions of these materials (Table 2) are permanganate-coloured; addition of water to the red pyridine complexes yields such coloured solutions. Long drying of the solvates at elevated temperatures *in vacuo* is necessary to remove the solvents; in some cases even heating at 140° *in vacuo* was ineffective.



(I)

In an attempt to find the features of the molecule responsible for anti-tumour activity a series of derivatives has been prepared where one hydroxyl group has been replaced by H, SMe, OMe, SH, Me, and Cl.

Thiele acetylation of 2,5-diphenyl-1,4-benzoquinone with perchloric acid as catalyst proceeded normally, provided the temperature of the reaction was controlled. Hydrolysis, followed by mild oxidation, of the resultant hydroxyquinol triacetate yielded the monohydroxyquinone (I; R = R′ = H).

Further reaction of this material with methanethiol gave the methylthio-derivative (I; R = H, R′ = SMe) directly. Addition of mercaptoacetic acid gave a recalcitrant product and it was necessary to purify the material through the leucoacetate. The free mercaptoquinone (I; R = H, R′ = SH) was extremely unstable and attempts to crystallize it led to decomposition. Alkylation of the monohydroxyquinone (I; R = R′ = H) with acetyl peroxide [4] furnished the hydroxymethylquinone (I; R = H, R′ = Me) in excellent yield. The other variants listed above were best prepared by metathesis from 2,5-dichloro-3,6-diphenylquinone (see Experimental section).

All the compounds prepared that lacked the central 2,5-dihydroxy-groups were inactive against the L1210 leukemia in mice and had negligible antibacterial activity. Also, simpler molecules such as 2,5-dihydroxyquinone and 2,5-dihydroxy-3-phenyl-1,4-benzoquinone proved inactive.

The necessity of retaining the dihydroxyquinone grouping suggests that biological efficacy could be dependent on one or more of the following properties: the chelating power, the redox potential, or the acidity of the α-hydroxyquinone system. Quantitatively the three properties are inter-related and depend on the electron-density over the quinone ring. Accordingly, a series of polyporic acid derivatives with electron-donating and -attracting substituents on one phenyl group has been prepared.

Of numerous compounds prepared by arylating quinones with diazonium salts,[5] a few have been examined for their antibacterial properties.[6] A method of preparing 2,5-dichloro-3-phenyl-1,4-benzoquinone, in acceptable yield on a reasonable scale, from benzene diazo-acetate and 2,5-dichlorobenzoquinone is given in the Experimental section. Coupling of this with substituted arenediazonium salts yields the diaryldichloroquinones (see Table 1) that are readily hydrolyzed in high yield to the dihydroxyquinones (Table 2). This route is very flexible, and the only limitation is the requirement of a diazotizable amine.

The second arylation consistently gave poor yields (0—35%) that were not increased by the methods listed by Fieser *et al.*[4] The yields depend on the substitution pattern of the amines (*para* > *meta* ⩾ *ortho*) but probably more on the solubility of the products than on steric and electronic factors.

Most of these diaryldihydroxyquinones have some anti-tumour activity but no correlation between structure and biological activity is obvious.

[4] Fieser *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 2060; 1948, **70**, 3151; Kvalnes, *Annalen*, 1934, **514**, 157; *J. Amer. Chem. Soc.*, 1934, **56**, 2478; 1948, **70**, 3201.
[5] Asano and Kameda, *J. Pharm. Soc. Japan*, 1939, **59**, 291.
[6] Asano and Huziwara, *J. Pharm. Soc. Japan*, 1939, **59**, 284.

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Experimental

Extraction of Sticta coronata.—This was carried out essentially as described by Murray [2] and gave calycin (2·95%), m. p. 243—244° (lit.,[2,6] 242—244°), pulvinic anhydride (0·63%), m. p. 225—226° (lit.,[2,7] m. p. 222—224°, and polyporic acid (1·4%), m. p. 305° (sublimes). Polyporic acid was compared directly with a synthetic specimen.[8]

2′,3′,5′-Triacetoxy-p-*terphenyl*.—To a suspension of 2,5-diphenyl-1,4-benzoquinone (10 g.) in acetic anhydride (65 ml.) 72% perchloric acid (1 ml.) was added dropwise with stirring. The suspension was kept at 55° until a homogeneous solution resulted. After a further 4 hr. at room temperature the excess of anhydride was decomposed with water, and the *triacetate* collected, m. p. 189—191° (9·6 g.). Repeated crystallization from methanol gave prisms, m. p. 192—193° (Found: C, 71·5; H, 4·9. $C_{24}H_{20}O_6$ requires C, 71·3; H, 5·0%).

3-Hydroxy-2,5-diphenyl-1,4-benzoquinone.—Sodium (1·8 g.) was added to a suspension of the above triacetate (10 g.) in absolute methanol (50 ml.), and the suspension stirred till homogeneous. Addition to a solution of ferric chloride hexahydrate (13·5 g.) in acetic acid (25 ml.) and concentrated hydrochloric acid (15 ml.) gave a deep red solution which deposited the *quinone* (6·3 g.) on addition of water (50 ml.). Crystallization from acetic acid gave scarlet prisms, m. p. 226—227° (Found: C, 78·1; H, 4·1. $C_{18}H_{12}O_3$ requires C, 78·2; H, 4·4%).

2-Hydroxy-5-methylthio-3,6-diphenyl-1,4-benzoquinone.—A solution of the hydroxyquinone (2 g.) in ethanol (1 l.) was treated with a ten-fold excess of methanethiol overnight. 2 Equivs. of ferric chloride in ethanol was then added, followed by concentrated hydrochloric acid (2 ml.). Dilution with water (2 l.) after a further 2 hr. precipitated the *methylthio-quinone*. Crystallization from small volumes of acetic acid gave vermilion needles (1·36 g.), m. p. 151—153° (Found: C, 70·9; H, 4·3; S, 10·1. $C_{19}H_{14}O_3S$ requires C, 71·1; H, 4·4; S, 10·0%).

2-Hydroxy-5-mercapto-3,6-diphenyl-1,4-benzoquinone.—Use of mercaptoacetic acid in place of methanethiol in the preceding experiment gave a crude product (2·1 g.) which was suspended in acetic anhydride (10 ml.) and refluxed with zinc dust (3 g.) for 10 min. Isolation in the usual manner gave a *tetra-acetate*, needles (from ethanol), m. p. 243—244° (Found: C, 65·4; H, 4·5; S, 6·4. $C_{26}H_{22}O_7S$ requires C, 65·1; H, 4·6; S, 6·7%). To a suspension of this (1·6 g.) in methanol (10 ml.), sodium (0·5 g.) was added and the solution was stirred at room temperature in air for 0·5 hr., then filtered and slowly acidified in the cold with just sufficient methanolic hydrogen chloride. The crimson precipitate was washed by suspension in water, collected, and stored *in vacuo*. Attempted recrystallization led to a dark brown insoluble material, presumably the disulphide since reductive acetylation re-formed the leucoacetate recorded above. On being heated, the *mercapto-quinone* gradually darkened but did not melt below 360° (Found: C, 70·0; H, 3·7; S, 10·1. $C_{18}H_{12}O_3S$ requires C, 70·1; H, 3·9; S, 10·4%).

2-Hydroxy-5-methyl-3,6-diphenyl-1,4-benzoquinone.—An acetic acid solution of 3-hydroxy-2,5-diphenylbenzoquinone (1·46 g.) was kept at 90—95° while freshly prepared ethereal acetyl peroxide (0·62 g. of peroxide) was introduced beneath the surface. Heating at 95° was continued until gas evolution ceased. Evaporation and crystallization from aqueous dioxan gave the *methyl-quinone* as orange-red needles (1·22 g.), m. p. 154—155° (Found: C, 78·3; H, 5·1. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·9%).

2,5-Dimethyl-3,6-diphenyl-1,4-benzoquinone.—This *compound* was prepared by using 2,5-diphenylbenzoquinone (2 g.) and 2 mol. of acetyl peroxide. It separated from aqueous dioxan in lemon-coloured needles, m. p. 146—147° (Found: C, 83·1; H, 5·5. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

2,5-Dichloro-1,4-benzoquinone.—A suspension of quinol (500 g.) in concentrated hydrochloric acid (2·5 l.) was stirred rapidly while powdered potassium chlorate (379 g.) was added portionwise so that the temperature remained between 40° and 45°. After 12 hr. at 0° the dichloroquinol was collected and immediately oxidized with sodium dichromate in aqueous sulphuric acid. The dichloro-quinone (476 g.) separated from ethanol in orange prisms, m. p. 158—160°.

2,5-Dichloro-3-phenyl-1,4-benzoquinone.—Aniline (65·7 ml.) in water (100 ml.) and concentrated hydrochloric acid (216 ml.) was diazotised with sodium nitrite (54·6 g.) in water (150 ml.), then added to a solution of 2,5-dichlorobenzoquinone (105·5 g.) in methanol (3·3 l.) and ether (900 ml.) with stirring while anhydrous sodium acetate (120 g.) in water (200 ml.) was added

[7] Hesse, *J. prakt. Chem.*, 1900, **62**, 334.
[8] Shildmeck and Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 2373.

at an equivalent rate, the temperature being kept below 40°, 100 ml. of water being used for rinsing. The solution was stirred for a further 2 hr., then solvent (1680 ml.) was removed by distillation through a short fractionating column. Hot water (900 ml.) was added and the boiling solution filtered rapidly. The required *quinone* separated on cooling. Crystallization from ethanol (charcoal) gave material (62 g.), m. p. 121—124°, suitable for further coupling. Repeated crystallization gave pure material as lemon-coloured plates, m. p. 127—128° (Found: C, 56·9; H, 2·4; Cl, 28·4. $C_{12}H_6Cl_2O_2$ requires C, 56·9; H, 2·4; Cl, 28·0%).

TABLE 1. 2,5-*Dichloro*-3-p-R-*phenyl*-6-*phenyl*-1,4-*benzoquinones*.

			Found (%)					Required (%)			
R	Solvent	M. p.	C	H	Cl	N	Formula	C	H	Cl	N
H	Bu^{n}OH	209—210° [a]	66·0	3·2	21·2	—	$C_{18}H_{10}Cl_2O_2$	65·7	3·1	21·0	—
OMe	EtOH	184—186 [b]	63·3	3·0	19·3	—	$C_{19}H_{12}Cl_2O_3$	63·5	3·1	19·7	—
Me	AcOH	212—213 [c]	66·4	3·6	20·7	—	$C_{19}H_{12}Cl_2O_2$	66·5	3·5	20·7	—
Cl	Bu^{n}OH	234—235	59·1	2·4	29·1	—	$C_{18}H_8Cl_4O_2$	59·4	2·5	29·3	—
SMe	EtOH	228—229	60·6	3·1	18·7	—	$C_{19}H_{12}Cl_2O_2S$	60·8	3·2	18·9	—
NHAc	AcOH	229—300	62·0	3·2	—	3·4	$C_{20}H_{12}Cl_2NO_3$	62·2	3·4	—	3·6
NMeAc	EtOH	245—246	63·0	3·8	—	3·5	$C_{21}H_{15}Cl_2NO_3$	63·0	3·8	—	3·5
NMe_2	AcOH–EtOH	193—194	64·6	4·2	—	3·7	$C_{20}H_{15}Cl_2NO_2$	64·5	4·1	—	3·7
$CO{\cdot}NH_2$	EtOH	283—284	61·0	3·0	—	3·3	$C_{19}H_{11}Cl_2NO_3$	61·3	3·0	—	3·8
$SO_2{\cdot}NH_2$	AcOH	284 [d]	52·9	2·9	—	3·1	$C_{18}H_{11}Cl_2NO_4S$	52·9	2·7	—	3·4
$SO_2{\cdot}Me$	EtOH	267—268	56·2	3·1	17·6	—	$C_{19}H_{12}Cl_2SO_4$	56·0	3·0	17·4	—
CO_2Me	MeOH	229—230	61·9	3·2	17·9	—	$C_{20}H_{12}Cl_2O_4$	62·0	3·1	18·3	—

[a] Kvalnes [4] gives m. p. 207—208°. [b] Lit.,[5] 183—185°. [c] Lit.,[5] 204—205°. [d] With decomp.

TABLE 2. *Polyporic acid derivatives* (I; R′ = OH).

			Found (%)				Required (%)		
R	Solvent	M. p.	C	H	N	Formula	C	H	N
H [a]	Toluene	305° (subl)	74·2	4·3	—	$C_{16}H_{12}O_4$	74·0	4·1	—
OMe	Pyridine	267—269	70·5	4·3	—	$C_{19}H_{14}O_5$	70·8	4·4	—
Me	Pyridine	259—260 [b]	74·3	4·5	—	$C_{19}H_{14}O_4$	74·5	4·6	—
Cl	Toluene	289—291	66·3	3·5	—	$C_{16}H_{11}ClO_4$	66·2	3·4	—
SMe	Pyridine	285—287	67·3	4·1	—	$C_{19}H_{14}O_4S$ [d]	67·5	4·2	—
NHAc	Pyridine	307—309	68·5	4·5	3·7	$C_{19}H_{13}NO_5$	68·8	4·3	4·0
NMeAc	Pyridine–ligroin	226—228	69·0	5·1	3·8	$C_{21}H_{17}NO_5$	69·4	4·7	3·9
NMe_2	Pyridine	241 [c]	71·4	5·0	4·1	$C_{20}H_{17}NO_4$	71·6	5·1	4·2
$CO{\cdot}NH_2$	Pyridine	>360	67·9	4·0	4·2	$C_{19}H_{13}NO_5$	68·1	3·9	4·2
$SO_2{\cdot}NH_2$	Pyridine	>360	61·1	3·9	6·5	$C_{23}H_{18}N_2O_6S$	61·3	4·0	6·2
$SO_2{\cdot}Me$	Bu^{n}OH	192—193	61·2	3·4	—	$C_{19}H_{14}O_6S$ [f]	61·6	3·7	—
CO_2Me	Dioxan–H_2O	324—328	68·5	4·2	—	$C_{20}H_{14}O_6$	68·6	4·0	—

[a] Polyporic acid. [b] Lit.,[5] 254°. [c] With decomp. [d] Found: S, 9·7. Reqd.; S, 9·5%. [e] Includes one mol. of pyridine of crystallization, not removed on drying *in vacuo*. [f] Found: S, 9·0. Reqd.: S, 8·7%.

The by-product remaining from the filtration was 2,5-dichloro-3,6-diphenyl-1,4-benzoquinone which crystallized from butan-1-ol as orange-yellow plates (11·1 g.), m. p. 209—210° (Kvalnes [4] gives m. p. 207—208°) (Found: C, 66·0; H, 3·2; Cl, 21·3. Calc. for $C_{18}H_{10}O_2Cl_2$: C, 65·7; H, 3·1; Cl, 21·0%).

2,5-*Diaryl*-3,6-*dichlorobenzoquinones*.—To a solution of the dichlorophenylbenzoquinone (5 g.) in ethanol (150 ml.) was added alternately a solution of the diazonium salt from 1·2 mol. of amine (prepared in the minimum volume of water) and a saturated solution of sufficient sodium acetate to neutralize the excess of acid. Alternatively an acetylnitrosoamine may be used instead of the diazotized amine. After 12 hr. the solution was heated to the b. p. and water added to turbidity. The crystals, oil, or tar obtained on refrigeration was dealt with according to its nature.

Hydrolysis of Dichloroquinones to Dihydroxyquinones.—To the pure dichloroquinone was added sufficient methanol to wet the crystals, followed by 10% aqueous sodium hydroxide (8 equiv.), and the suspension stirred until a solution resulted, for which occasionally mild heating was required. After dilution with an equal volume of water the solution was filtered and strongly acidified, and the *hydroxyquinone* collected and crystallized (see Table 2). The m. p. depend on the rate of heating and are not always sharp. The figures quoted were obtained with heating at 2°/min. from 20° below the m. p.

2-Chloro-5-methoxy-3,6-diphenyl-1,4-benzoquinone.—Sodium methoxide (1 mol.) in methanol was added with stirring to a solution of dichlorodiphenylbenzoquinone (2 g.) in methanol. Evaporation to incipient separation and cooling gave the *product* (1·6 g.), orange-red prisms (from di-n-pentyl ether), m. p. 180—181° (Found: C, 70·8; H, 4·1; Cl, 10·4. $C_{19}H_{13}O_3Cl$ requires C, 70·3; H, 4·0; Cl, 10·9%).

2-Hydroxy-5-methoxy-3,6-diphenyl-1,4-benzoquinone.—To the chloromethoxyquinone (2 g.) in aqueous dioxan was added 10% aqueous sodium hydroxide (2 mol.), and the mixture heated on the water-bath for 1 hr., diluted with an equal volume of water, filtered, and acidified. Crystallization from aqueous dioxan gave the *hydroxyquinone* as chocolate-brown needles (1·36 g.), m. p. 210—211° (Found: C, 74·3; H, 4·8. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

2,5-Dimethoxy-3,6-diphenyl-1,4-benzoquinone.—This *compound*, prepared from the corresponding dichloroquinone by the action of 2 mols. of methanolic sodium methoxide in quantitative yield, crystallized from acetic acid, in red, diamond-shaped plates, m. p. 202—203° (Found: C, 75·9; H, 4·8; OMe, 18·9. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0; 2OMe, 19·4%).

2-Chloro-5-hydroxy-3,6-diphenyl-1,4-benzoquinone.—Solutions of the dichlorodiphenylquinone (2 g.) in dioxan, and potassium hydrogen carbonate (0·6 g.) in water, were mixed and heated for 4 hr. on the water-bath; the whole was filtered after addition of an equal volume of water and then acidified. The *product* separated from dioxan in yellow needles (1·28 g.), m. p. 211—212° (Found: C, 70·0; H, 3·4; Cl, 11·4. $C_{18}H_{11}O_3Cl$ requires C, 69·6; H, 3·6; Cl, 11·4%).

Thanks are offered to Dr. R. Cooper of the Auckland Institute and Museum for assistance in collection and identification of source material, and to Dr. J. F. Burton of this laboratory for details of the biological testing. Microanalyses are by Dr. Campbell of the microchemical laboratory, University of Otago. The above research was supported by the Auckland Division of the New Zealand Branch of the British Empire Cancer Campaign Society (Inc.).

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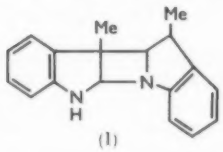
194. *Indoles. Part V.* 3-Alkylindole Dimers.*

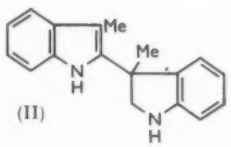
By G. F. SMITH and A. E. WALTERS.

Structure (III) is proposed for the skatole dimer. The action of mineral acid on 2-methyl-, 3-n-propyl-, 3-isopropyl-, and 3-t-butyl-indole, and on tryptamine is discussed.

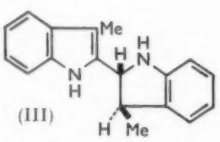
ODDO and CRIPPA [1] found that skatole is converted in high yield into a dimer by the action of dry hydrogen chloride in ether. They assigned structure (I) to the dimer. Schmitz-Dumont [2] showed the presence in it of an indole and of an indoline nucleus and, on insufficient experimental evidence, proposed structure (II).



(I)



(II)



(III)

We have obtained degradative evidence which shows skatole dimer to have structure (III). (The stereochemistry shown is based only on a theoretical argument; see below.) The dimer forms a methyl-methiodide, which is cleaved by sodium in liquid ammonia to a base, $C_{20}H_{21}N_2$, characterised as the crystalline picrate: the base is oxidised by chromic

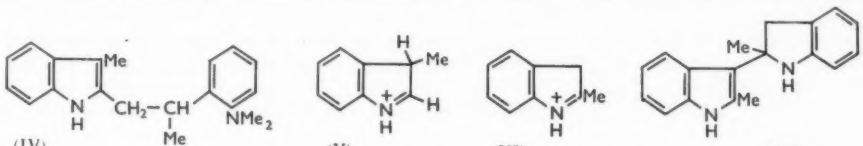
* Part IV, *J.*, 1960, 4574.

[1] Oddo and Crippa, *Gazzetta*, 1924, **54**, 339; Oddo, *ibid.*, 1933, **63**, 898.
[2] Schmitz-Dumont, *Annalen*, 1934, **574**, 267.

acid to methylsuccinic acid. This, together with the observations that the base has an ultraviolet spectrum indicative of an aromatic indole nucleus, that it does not give a colour with Ehrlich's reagent, and that it is derived from two mol. of skatole, can only be interpreted in terms of structure (IV), which leads to structure (III) for the original dimer. Attempts to carry out the Hofmann degradation of the skatole dimer along the lines used for the indole dimer [3] were unsuccessful.

The mechanism of dimerisation can be visualised as attack by the electrophilic iminium carbon atom in ion (V) on position 2 of an unprotonated skatole molecule. Attack by the less hindered side of cation (V) will be favoured, leading to the stereochemistry shown in structure (III).

It is of interest that 2-methylindole cannot be made to dimerise: [2] the main reason for this is almost certainly the reduced electrophilic character of the iminium carbon atom in



(IV) (V) (VI) (VII)

ion (VI), in comparison with the corresponding atom in ion (V), owing to the electron-releasing nature of the methyl group, possibly coupled with a steric hindrance effect; it is paralleled by the lower electrophilic activity of methyl ketones than of aldehydes. That the failure of 2-methylindole to dimerise is not due to a lower susceptibility of position 3 to electrophilic attack is proved by the formation of mixed dimers between 2-methylindole and indole and between 2-methylindole and skatole in which the 2-methylindole moiety retains its aromaticity: [4] this means that 2-methylindole is susceptible to electrophilic attack by the normally reactive 3-protonated 2-unsubstituted indole cations.

The product which 2-methylindole would form if it dimerised, base (VII), has been prepared by Witkop and Patrick [5] by reducing the 2-methylindole autoxidation product with lithium aluminium hydride. We have found that base (VII) parallels the indole dimer in that it dissociates on dry distillation at ordinary pressure to two mol. of 2-methylindole (in 68% yield): the dimer (III) is thermally much more stable, for it can be distilled largely unchanged. This dimer (III) does, however, dissociate under acid-catalysis: distillation of a solution of the dimer in dilute hydrochloric acid leads to skatole in 91% yield (1·82 mol.).

We have explored the limitations of the dimerisation reaction in various 3-substituted indoles. We find that dimerisation is markedly subject to steric hindrance. Thus, whereas, as might be expected, 3-n-propylindole dimerises as easily as skatole (the reported failure of 3-ethylindole to dimerise [6] must be an error), neither 3-isopropylindole nor 3-t-butylindole dimerises. This failure is most probably due to steric hindrance of approach of the electrophilic reagent to position 2 by the bulky 3-substituent in the unprotonated molecule. On the other hand models show that approach of a nucleophilic reagent to position 2 of a 3-protonated molecule is quite open: it should therefore be possible to produce mixed dimers; for instance, indole and 3-t-butylindole should give 2-methyl-3-(3-t-butyl-2-indolinyl)indole.

Dimerisation is also prevented by the presence of a formal positive charge in the 3-side-chain: thus tryptamine cannot be dimerised. Even after one month at 15° in 15% aqueous hydrochloric acid, tryptamine was recovered completely unchanged (complications due to autoxidation were avoided by working in an evacuated sealed tube; under

[3] Hodson and Smith, *J.*, 1957, 3544.
[4] Noland and Hammer, *J. Org. Chem.*, 1960, **25**, 1525.
[5] Witkop and Patrick, *J. Amer. Chem. Soc.*, 1951, **73**, 713.
[6] Schmitz-Dumond and Geller, *Ber.*, 1933, **66**, 766.

XUM

the same conditions, an 85% yield of the skatole dimer was obtained after 4 days); this cannot be due to a steric effect in view of the ease with which the isosteric 3-n-propylindole dimerises, but must be due to a field effect of the side-chain ammonium-nitrogen atom which prevents protonation at position 3, the first step in a dimerisation.

3-n-Propylindole, first prepared as a liquid by Brown *et al.*,[7] has now been obtained crystalline (m. p. 29°) by reduction of 3-propionylindole with lithium aluminium hydride. 3-t-Butylindole is a new compound (m. p. 67—68°) and was synthesised by the action of t-butyl bromide on indolylmagnesium bromide.

Experimental

trans-1,1,3-*Trimethyl*-2-(3-*methyl*-2-*indolyl*)*indolinium Iodide* (*Skatole Dimer Methyl-methiodide*).—A mixture of the skatole dimer (3 g.), dry acetone (100 c.c.), methyl iodide (10 g.), and anhydrous potassium carbonate (10 g.) was refluxed for 18 hr. The acetone and excess of methyl iodide were then boiled off, and the residue was washed with ether and then with cold water. Crystallisation of the residual solid from ethanol yielded the pure *iodide* as prisms, m. p. 211—212° (3·9 g., 82%) (Found: C, 57·3; H, 5·7; N, 6·75. $C_{20}H_{23}IN_2$ requires C, 57·5; H, 5·6; N, 6·7%), $\lambda_{max.}$ 221, 277, and 292 (infl.) mμ (ε 55,000, 13,300, and 11,000 respectively) in EtOH.

2-(2-o-*Dimethylaminophenylpropyl*)-3-*methylindole* (IV).—A solution of the above iodide (520 mg.) in dry liquid ammonia (100 c.c.) was treated with an excess of freshly cut sodium, and the blue solution left for 1½ hr. The excess of sodium was then decomposed by the addition of ammonium chloride, the ammonia was allowed to evaporate, and the residue was partitioned between ether and water. The ether solution yielded a pale yellow viscous liquid (350 mg., 96%). This was treated with a solution of picric acid (275 mg.) in ethanol; a picrate crystallised (463 mg., 74%). Recrystallisation from ethanol gave the pure *picrate* as yellow prisms, m. p. 175—176° (Found: C, 60·3; H, 5·4; N, 13·2. $C_{26}H_{27}N_5O_7$ requires C, 59·9; H, 5·2; N, 13·4%), $\lambda_{max.}$ 283·5 and 292 mμ (ε 9400 and 8900) in EtOH.

Oxidation of base (IV). A solution of the above base (recovered from the picrate) (1·2 g.) and of chromium trioxide (10 g.) in 10% sulphuric acid (100 c.c.) was heated on the steam-bath for 1 hr. Excess of oxidising agent was reduced by sulphur dioxide, and the mixture extracted with ether (3 × 50 c.c.). The extracted material (40 mg.) was partially crystalline; it was refluxed in ethanol (4 c.c.) containing one drop of sulphuric acid for 3 hr., most of the ethanol was removed *in vacuo*, and the residue partitioned between ether and water. The ether extract yielded a pleasant smelling liquid (47 mg.), a solution of which in dry ether was added to anilinomagnesium bromide (prepared from 93 mg. of aniline) in ether. The mixture was refluxed for 30 min., then treated with excess of dilute hydrochloric acid, and the whole thoroughly extracted with ether. The extract yielded a partially crystalline product (58 mg.), crystallisation of which from aqueous ethanol yielded methylsuccindianilide as needles, m. p. and mixed m. p. 199° (25 mg.).

3-*n-Propylindole*.—3-Propionylindole (3·8 g.) was added to a solution of lithium aluminium hydride (1·0 g.) in ether (100 c.c.), and the mixture refluxed for 5 hr. Working up in the usual manner yielded the crude 3-n-propylindole as a pale yellow oil (3·3 g.). The product distilled at 153—154°/15 mm. and crystallised from pentane at 0°, to give the pure 3-*n-propylindole* as needles, m. p. 29° (Found: C, 82·8; H, 8·3. $C_{11}H_{13}N$ requires C, 83·0; H, 8·2%), $\lambda_{max.}$ 224, 281, and 291 mμ (ε 32,200, 5700, and 5100 respectively) in EtOH. The infrared spectrum was identical with that of non-crystalline 3-n-propylindole obtained by hydrogenation of 3-allylindole.[8]

Dimerisation of 3-*n-Propylindole*.—A solution of 3-n-propylindole (0·52 g.) in dry ether (100 c.c.) was treated with a slow stream of pure dry hydrogen chloride for 2 hr. The pink crystals which separated were filtered off and partitioned between aqueous sodium hydroxide and ether. The ether layer yielded the dimer as a pale yellow viscous liquid (0·45 g., 87%), $\lambda_{max.}$ 226, 285, and 292 mμ (ε 40,700, 13,200, and 12,300 respectively) in EtOH. The *hydrochloride* of this dimer crystallises from a small volume of ethanol as needles, m. p. 160—162° (Found: C, 74·1; H, 7·8; Cl, 10·0. $C_{22}H_{27}ClN_2$ requires C, 74·4; H, 7·7; Cl, 10·0%).

[7] Brown, Jones, and Henbest, *J.*, 1952, 3174.
[8] Brown, Ph.D. Thesis, Manchester, 1951.

3-*t-Butylindole*.—A stirred solution of indolylmagnesium bromide (from 19·2 g. of indole) in di-isopropyl ether (100 c.c.) was slowly treated with a solution of t-butyl bromide (21 c.c.) in di-isopropyl ether (50 c.c.). The mixture was stirred for 15 hr. under reflux, the Grignard complex decomposed with ammonium chloride solution, and the organic layer separated. This yielded a brown viscous liquid (26·4 g.) which distilled over a wide range (128—169°/9 mm.). The highest fraction, b. p. 158—169°/9 mm., was carefully redistilled to give a fraction, b. p. 166—169°/9 mm. (3·9 g.), which in benzene afforded a *picrate* (5·5 g.), as red needles, m. p. 105·5—107° (from benzene) (Found: C, 53·3; H, 4·4; N, 13·4. $C_{18}H_{18}N_4O_7$ requires C, 53·7; H, 4·5; N, 13·9%).

Decomposition of the picrate between aqueous ammonia and ether, and filtration of the ether solution through a column of alumina, yielded the crystalline base. Recrystallisation from pentane gave pure 3-*t-butylindole* as polyhedra, m. p. 67—68° (Found: C, 82·9; H, 8·7; N, 7·9. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%), $\lambda_{max.}$ 222·5 and 282·5 mμ (ε 32,600 and 5560) in EtOH.

We thank Dr. B. Witkop for a specimen of the base (VII). One of us (A. E. W.) is indebted to the D.S.I.R. for a Maintenance Award.

Department of Chemistry, The University, Manchester, 13. [*Received, July 25th*, 1960.]

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195. *Tracer Studies in Ester Hydrolysis. Part IX.* Phenyl and Diphenylmethyl Trifluoroacetate.*

By C. A. Bunton and T. Hadwick.

The acyl–oxygen bond is broken during hydrolysis of phenyl trifluoroacetate in acid, alkaline, or initially neutral aqueous dioxan. The kinetic forms of the hydrolysis are similar to those observed for methyl trifluoroacetate. The rate of acid hydrolysis is at a maximum when the concentration of acid is *ca.* 1·5M.

The alkaline hydrolysis of diphenylmethyl trifluoroacetate is by mechanism $B_{Ac}2$. Tracer and kinetic experiments prove the existence of mechanisms $B_{Ac}2$ and $B_{Al}1$ for hydrolysis in initially neutral solution, and of mechanisms $A_{Ac}2$ and $A_{Al}1$ for acid hydrolysis.

Hydrolysis of methyl trifluoroacetate is very rapid in alkaline solution.[1] It is not strongly catalysed by hydrogen ions, in comparison with unfluorinated esters, and the rate begins to level off at $[HClO_4] > 1M$, this unusual kinetic form being thought to be caused by a negative salt effect of the fully ionised perchloric acid. The acyl–oxygen bond was broken in acid, alkaline, and initially neutral solution.

Although we found exclusive acyl–oxygen fission for hydrolysis it is possible to observe bimolecular attack upon the methyl group by methoxide ion in absolute methanol. Traynham and Battiste [2] reported the rapid formation of a gas, thought to be dimethyl ether, in this reaction, and one of us has confirmed this by the use of gas–liquid chromatography. The mechanism must be $B_{Al}2$. Another example of alkyl–oxygen fission, probably with carbonium-ion formation, is the elimination of olefins during solvolyses of t-alkyl trifluoroacetates.[3]

The hydrolyses of phenyl and diphenylmethyl trifluoroacetate were studied by the methods applied to the methyl ester,[1] *i.e.*, determination of the kinetic forms of hydrolysis and of the position of bond fission. Because the mechanisms are strikingly different for

* Part VIII, *J.*, 1960, 3364.

[1] Bunton and Hadwick, *J.*, 1958, 3248.
[2] Traynham and Battiste, *J. Org. Chem.*, 1957, **22**, 1551.
[3] Moffat and Hunt, *J. Amer. Chem. Soc.*, 1958, **80**, 2985.

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differing alkyl groups, we discuss the results for the phenyl and the diphenylmethyl ester separately.

Phenyl Trifluoroacetate.—Hydrolysis is by acyl–oxygen bond fission (see p. 952). This position of bond fission appears to be universal for hydrolyses of phenyl esters. The rate of hydrolysis is increased by addition of alkali or acid, but whereas the effect of acid is comparatively small that of alkali is so great that the reaction in the presence of sodium hydrogen carbonate is too fast for measurement by conventional methods (see p. 951). The kinetic effects of added salts and acids are given in Table 1. Neutral salts decrease

TABLE 1. *Rates of hydrolysis of phenyl trifluoroacetate.*

Solvent: dioxan–water (70 : 30 v/v). Temp. 0°. Titration method (1), unless otherwise specified.

Initially neutral:

10^3k_1 (sec.$^{-1}$) 5·27, 5·59, 5·66, 5·85,[a] 5·96,[a] 6·15,[a] 11·4 [b] (mean value 10^3k_1 = 5·55 sec.$^{-1}$).

Effect of added salt:

$[LiClO_4]$ (M)	1·03	1·54	$[p\text{-}C_6H_4Me\cdot SO_3Na]$ (M)	0·384	0·565	$[CF_3\cdot CO_2K]$ (M)	0·715	1·01
10^3k_1 (sec.$^{-1}$)	3·50	2·19	10^3k_1 (sec.$^{-1}$)	3·24	2·80[c]	10^3k_1 (sec.$^{-1}$)	4·91	4·39

Acid solutions:

$[HClO_4]$ (M)	0·202	0·503	0·540	0·573	0·923	1·47	1·81	2·39	2·69	3·29	4·90
10^3k_1 (sec.$^{-1}$)	7·92	11·5[a]	10·4	8·64[d]	11·7	11·3[a]	8·18	6·00[a]	3·68	1·89	0·32
$[p\text{-}C_6H_4Me\cdot SO_3H]$ (M)	0·450	0·578	0·814	1·80	2·53	2·53					
10^3k_1 (sec.$^{-1}$)	9·21	8·62[a]	9·21	11·7	7·05[a]	7·67					

[a] Titration method (2). [b] Temp. 13·7°. [c] Slight pptn. during run. [d] $[LiClO_4]$ 0·765 M.

the rate, as was found for methyl trifluoroacetate.[1] The negative salt effects are in the sequence, sodium toluene-*p*-sulphonate > lithium perchlorate > potassium trifluoroacetate. Although the mechanism of this retardation is not completely understood,

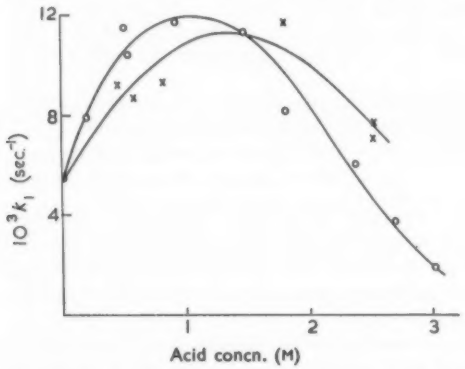

FIG. 1. *Hydrolysis of phenyl trifluoroacetate at 0°.*

○ *Perchloric acid.*
× *Toluene-p-sulphonic acid.*

these salts will decrease the activity of the water and probably reduce the activity coefficient of the ester [4] (*i.e.*, " salt in " the ester).

The kinetic form in acid is very similar to that observed for the hydrolysis of methyl trifluoroacetate, but, because our analytical method allowed rate measurements at comparatively high concentrations of acid, we were able to demonstrate the existence of a maximum rate of hydrolysis at $[HClO_4]$ or $[C_6H_4Me\cdot SO_3H]$ *ca.* 1·5M (Fig. 1). Because neutral salts decrease the rate of the neutral hydrolysis, it is difficult to calculate the rate constant for the acid-catalysed component of the hydrolysis. The ions of the added acids will have a negative salt effect upon the neutral hydrolysis, and probably also upon the acid hydrolysis. We were able to treat the hydrolysis of methyl trifluoroacetate semi-quantitatively, by assuming that the negative salt effects of perchloric acid were the same

[4] Long and McDevitt, *Chem. Rev.*, 1952, **51**, 119; Waind, *J.*, 1954, 2879.

as those of sodium perchlorate, and that these effects varied linearly with salt concentration over a limited range of concentration.[1] These approximations are less satisfactory for the experiments on phenyl trifluoroacetate in which we use concentrations of acid up to *ca.* 3M. An additional complication is that we were unable to estimate the initial slope of a plot of the first-order rate constant, k_1, against the acid concentration (Fig. 1) with precision, because the values of k_1 are scattered. Therefore we used an alternative method of calculation which is described in an Appendix. We assume that the logarithm of the rate of the acid and the neutral hydrolyses will be a linear function of ionic strength,[5] and that the negative salt effects upon the neutral hydrolysis will be the same for perchloric acid as for lithium perchlorate. This calculation, as applied to the acid hydrolysis of methyl trifluoroacetate, gives values for the rate constants close to those calculated earlier.[1]

The values of k_a (the second-order rate-constant for acid hydrolysis) are for perchloric $10^3k_a = 21$ (sec.$^{-1}$ mole^{-1} l.), and for toluene-*p*-sulphonic acid $10^3k_a = ca.\ 16$ (sec.$^{-1}$ mole^{-1} l.). The smaller catalysis by toluene-*p*-sulphonic acid accords with the observation that it is weaker than perchloric acid in water,[6] and it may not be fully dissociated in aqueous dioxan.

The Arrhenius equation for the neutral hydrolysis in dioxan–water (70 : 30 v/v) is $k_1 = 10^{4\cdot4} \exp(-8300/\boldsymbol{R}T)$ sec.$^{-1}$. The corresponding equations for the neutral hydrolyses of the methyl esters are: in dioxan–water (70 : 30 v/v) $k_1 = 10^{3\cdot6} \exp(-10{,}500/\boldsymbol{R}T)$ sec.$^{-1}$; and in dioxan–water (60 : 40 v/v) $k_1 = 10^{3\cdot8} \exp(-10{,}200/\boldsymbol{R}T)$ sec.$^{-1}$. (In an earlier paper incorrect values were given for the non-exponential Arrhenius parameter.[1])

Electron-withdrawal by the fluorine atoms should reduce the energy of activation for nucleophilic attack upon the acyl-carbon atom. The low value of the non-exponential Arrhenius parameter, corresponding to a negative entropy of activation ($\Delta S^* = -40$ e.u. for hydrolysis of phenyl trifluoroacetate), suggests that there is considerable orientation of water molecules in the transition state, more than in the initial state. This is probably because the transition state is akin to that for addition to a carbonyl carbon atom.[7]

Diphenylmethyl Trifluoroacetate.—Because of the known stability of the diphenylmethyl cation,[8] we expected to observe at least some alkyl–oxygen fission in acid and neutral hydrolyses of this ester (cf. refs. 9 and 10).

The position of bond fission was determined by isolating diphenylmethanol after hydrolysis with water enriched in oxygen-18. A base, 2,6-lutidine, was added for the neutral hydrolyses, to suppress the exchange between diphenylmethanol and water which would be catalysed by trifluoroacetic acid liberated during reaction. (2,6-Lutidine is one of several tertiary amines which can be used as non-nucleophilic buffers.[11])

The acid hydrolysis is faster than the oxygen exchange of diphenylmethanol, and a small correction for the latter, based on control experiments, was applied. Our tracer experiments (Table 2) show that the acyl–oxygen bond is broken during alkaline hydrolysis, but mixed bond fission is found for hydrolysis in acid and initially neutral solution. The position of the bond fission depends, not only upon the nature of the reagent, but also upon the temperature and the solvent, and for an understanding of the mechanisms it is necessary to consider the bond fission and the kinetic form together. We discuss the mechanisms of neutral and acid hydrolysis separately.

The first-order rate constants, k_1, for the neutral hydrolyses are given in Table 3. These refer to two concurrent reactions with different positions of bond fission; the amount

[5] Frost and Pearson, "Kinetics and Mechanism," Chapman and Hall, London, 1953, p. 140.
[6] Bascombe and Bell, *J.*, 1959, 1096.
[7] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626; 1953, **75**, 5986.
[8] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 325.
[9] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203; Harvey and Stimson, *J.*, 1956, 3629; Bunton and Hadwick, *J.*, 1957, 3043.
[10] Bunton, Day, Flowers, Sheel, and Wood, *J.*, 1957, 963.
[11] Long and Pritchard, *J. Amer. Chem. Soc.*, 1957, **79**, 2365.

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of alkyl–oxygen fission varies from 6% in dioxan–water (60 : 40 v/v) at 25·0°, to 37% in this solvent at 72·9° (Table 2). We can expect the unimolecular alkyl–oxygen fission, $B_{Al}1$, to be favoured relatively to the bimolecular acyl–oxygen fission, $B_{Ac}2$, by the factors which favour carbonium-ion formation. Those relevant to our experiments are temperature and solvent composition. Many, though not all, unimolecular processes have higher activation energies than their bimolecular counterparts, and the extent of alkyl–oxygen bond fission increases, as expected, with increasing temperature (Table 2). Somewhat

TABLE 2. *Bond fission for diphenylmethyl trifluoroacetate.*

The enrichments of the control samples are given in parentheses.*
Neutral solution: Isotopic abundance of solvent water = 0·863 atom % excess.

Solvent (Dioxan vol. %)	Temp.	Isotopic abundance of product (atom % excess)	Alkyl–oxygen fission (%)
40	72·9°	0·275 (0·014)	30 [a, b]
60	,,	0·336 (0·016)	37 [b]
,,	44·6	0·117 (0·017)	12
,,	25·0	0·060 (0·011)	6
70	72·9	0·220 (0·020)	23 [b]

[a] Ester only partially soluble. [b] For experiments at 72·9° the warming-up time is not negligible relatively to the half-life of reaction. These values therefore underestimate the amount of alkyl–oxygen bond fission.

Perchloric acid: in dioxan–water (60 : 40 v/v).

Temp.	$[HClO_4]$ (M)	Isotopic abundances (atom % excess) H_2O	ROH	Alkyl–oxygen fission (%)
25°	1·0	0·776	0·368 (0·038)	42
,,	2·0	0·680	0·428 (0·104)	48
44·6	1·0	0·776	0·531 (0·055)	62

Alkaline hydrolysis: in water.
Isotopic abundance of water 0·863, of product 0·014 atom % excess.

* For the control tests the diphenylmethanol, with the equivalent amount of trifluoroacetic acid, was kept under the hydrolysis conditions for *ca.* 6 half-lives of the hydrolysis.

TABLE 3. *Rates of hydrolysis of diphenylmethyl trifluoroacetate.*

Dioxan–water (60 : 40 v/v), unless otherwise specified.

Initially neutral solution:

Temp.	0°	10·4°	25·0°	35·8°	42·5°
[Salt] (M)	—	—	—	—	—
10^5k_1 (sec.$^{-1}$)	0·627	2·10	9·14, 9·44	30·2	72·5

Temp.	25°							
[Salt] (M)	$CF_3{\cdot}CO_2K$	0·202	0·561	1·00	$LiClO_4$	0·194	0·820	—
10^5k_1 (sec.$^{-1}$)		10·1	8·83	7·54		14·4	32·0	2·81 [a]

Acid solution: (Temp. 25° unless otherwise specified.)

$[HClO_4]$ (M)	0·197	0·365	0·784	0·983	1·02	1·36	1·63	2·00	0·936	1·69	1·06	1·49	1·80
10^5k_1 (sec.$^{-1}$)	24·2	35·3	84·8	160 [b]	121	180	253	383	7·95 [c]	15·0 [c]	60·5 [a]	104 [a]	160 [a]

[a] Dioxan–water (70 : 30 v/v). [b] 0·51M-$LiClO_4$ added. [c] At 0°.

similarly, the amount of alkyl–oxygen bond fission increases with increasing water content of the solvent, because carbonium-ion formation, with charge separation, is facilitated.[12]

The temperature-dependence of the bond fission shows that the unimolecular mechanism, $B_{Al}1$, has a higher activation energy than the bimolecular mechanism, $B_{Ac}2$, and a plot of log k_1 against the reciprocal of the absolute temperature is not a straight line, but a smooth curve with slope increasing with temperature. This can be seen from the variation of the values of E (the Arrhenius activation energy) with temperature. The following

[12] Ref. 8, p. 345.

values are calculated over the preceding 10° for neutral hydrolysis in dioxan–water (60 : 40 v/v):

Temp.	10°	20°	30°	40°
E (kcal. mole^{-1})	17·2	18·3	19·5	20·6

These activation energies are considerably greater than those for the neutral hydrolyses of methyl [1] and phenyl trifluoroacetates (p. 945).

It should be possible, in principle, to use the temperature-dependence of the bond fission to calculate the difference in activation energies for the two mechanisms. This has not been done here, because the fastest measured reaction rate corresponds to only 12% of alkyl–oxygen bond fission, and this figure is uncertain because we do not know whether 2,6-lutidine affects the rate, and we know that trifluoroacetate ions, formed during reaction, do (p. 946). However it is clear that the activation energy for the unimolecular mechanism, $B_{Al}1$, must be considerably greater than 21 kcal. mole^{-1}, as expected for such a reaction.

The effects of added neutral salts confirm this picture of two simultaneous reactions. Azide ions intervene by trapping diphenylmethyl ions formed during hydrolysis by mechanism $B_{Al}1$ (Table 4); the extent of intervention in the hydrolysis of diphenylmethyl chloride is given there for comparison.

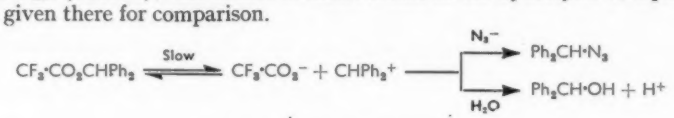

TABLE 4. *Azide intervention.*

Solvent dioxan–water (60 : 40 v/v), unless otherwise specified.

Temp.	25°			72·9°	100°	
[NaN_3] (M)	0·38	0·31 *	0·38 *	0·33	0·30	0·16
[$Ph_2CH{\cdot}N_3$] (mole %)	14	62	65	35	37	26 †

* Ph_2CHCl. † Dioxan–water (70 : 30 v/v).

Just as an increase in temperature increases the extent of alkyl–oxygen bond fission, so it increases carbonium-ion capture by azide ions. There are two reasons for this; first the proportion of reaction by mechanism $B_{Al}1$ increases with increasing temperature, and, secondly, there is a difference of *ca.* 4 kcal. mole^{-1} between the activation energies for carbonium-ion capture by azide ions and by water,[13] *i.e.*, azide ion is a more effective competitor at higher temperatures. For a given temperature, the extent of azide-ion intervention is greater for the more aqueous solvent, with its greater component of $B_{Al}1$. (The competitive efficiency of the azide ion is little affected by changes in the water content of the solvent.)

It should also be possible, in principle to use these intervention experiments to calculate the proportion of mechanism $B_{Al}1$, by finding the competitive efficiency of azide, relative to water, from the experiments on a diphenylmethyl halide. Comparison between the extents of azide intervention in hydrolysis of the chloride and the trifluoroacetate (Table 4), suggests that there is *ca.* 20% of carbonium-ion formation for hydrolysis of the latter at 25°, in the presence of 0·38M-sodium azide. This is much larger than the amount of alkyl–oxygen fission (with carbonium-ion formation), as determined by use of ^{18}O, in the absence of sodium azide (Table 2). It is probable that this salt is favouring carbonium-ion formation, by an ionic-strength effect, and at the same time it may retard hydrolysis by mechanism $B_{Ac}2$, because neutral salts retard the neutral hydrolysis of methyl and phenyl trifluoroacetates by mechanism $B_{Ac}2$ (p. 944).

Lithium perchlorate and trifluoroacetate both have kinetic salt effects upon the neutral hydrolysis. Their forms are very different from those observed for methyl [1] and phenyl trifluoroacetate (p. 944), whose neutral hydrolyses were retarded by these salts. Lithium

[13] Hawdon, Hughes, and Ingold, *J.*, 1952, 2499.

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perchlorate increases the total rate of neutral hydrolysis of diphenylmethyl trifluoroacetate. Increase in ionic strength will facilitate the charge formation which occurs during neutral hydrolysis, and this accelerating effect must outweigh any negative salt effect upon mechanism $B_{Ac}2$.

The behaviour of lithium trifluoroacetate is more complex. The rate of hydrolysis first increases, and then decreases, on addition of this salt (Table 3). Such behaviour has been observed with chloride ions in the S_N1 solvolysis of 2,3-dichlorodioxan,[14] and it was thought to be the result of an ionic-strength acceleration predominating, at low ion concentration, over a retarding common-ion effect. Such an explanation is probably correct for our results, although we have the complication of an extra component of reaction ($B_{Ac}2$) which will show no common-ion retardation.

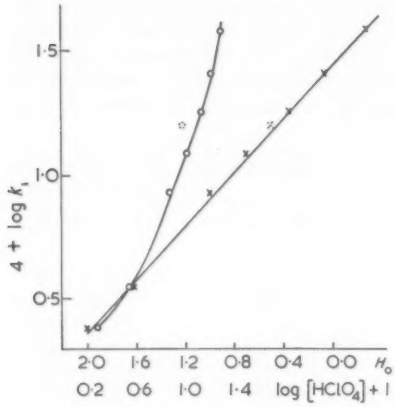

FIG. 2. *Acid-catalysed hydrolysis of diphenylmethyl trifluoroacetate at 25°.*

○ *Plot of* log k_1 *against* log [$HClO_4$].
× *Plot of* log k_1 *against* H_0.
0·51M-$LiClO_4$ *present for broken circle and cross.*

The extent of acid catalysis (relative to the neutral rate) is not large by comparison with that usually found for ester hydrolyses, but it is greater than for hydrolyses of other trifluoroacetates (ref. 1 and p. 944). The isotopic results again show two simultaneous reaction paths, one with acyl–oxygen and the other with alkyl–oxygen bond fission (Table 2). As for neutral hydrolysis, the extent of alkyl–oxygen bond fission increases with temperature, and it seems that mechanisms $A_{Al}1$ and $A_{Ac}2$ co-exist, the former having the higher activation energy.

It is usually found that the rates of specific hydrogen-ion catalysed hydrolyses are, to a first approximation, proportional to the acid concentration in bimolecular or to Hammett's acidity function, h_0, in unimolecular reactions [15] (although intermediate kinetic forms are known). Our acid hydrolyses fit neither of these limiting forms: the plot of log k_1 against the logarithm of perchloric acid concentration is a curve of continually increasing slope, always greater than unity; whilst against $-H_0$ it is a straight line of slope 0·55 (Fig. 2). From the bond-fission results this must be an example of two simultaneous reactions of different kinetic forms. The unimolecular mechanism $A_{Al}1$ should increase in relative importance at higher acid concentrations (where h_0 diverges from [$HClO_4$]), and the rate of the bimolecular mechanism, $A_{Ac}2$ may increase more slowly than does [$HClO_4$]. [This behaviour is observed for the acid hydrolyses of the methyl [1] and phenyl trifluoroacetate (Fig. 1).]

Tracer experiments (Table 2) prove that the relative importance of mechanism $A_{Al}1$ increases with increasing [$HClO_4$]. If we could measure the rate at acid concentrations

[14] Salomaa, *Acta Chem. Scand.*, 1954, **8**, 744.
[15] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

> *ca.* 3M, we should expect to find the rate varying linearly with h_0. Unfortunately our dilatometric method fails at *ca.* 2M-$HClO_4$ and we could not test this point. However, we found that at a lower temperature (0°) the slope of log k_1 against $-H_0$ was only 0·3 (from results in Table 3); this is understandable because reaction $A_{Al}1$, whose rate follows h_0, will be relatively unimportant at this temperature.

It has been suggested that the values of the entropy, ΔS^*, or the energy, E, of activation provide a test of molecularity, and in particular that ΔS^* is negative for bimolecular reactions, and near to zero, or positive, for unimolecular ones.[16]

We find changes in the values of ΔS^* and E in the expected direction, with increasing acid concentration:

$[HClO_4]$ (M)	E (kcal. mole^{-1})	ΔS^* (e.u.)
0·936	16·8	−18·2
1·69	18·9	−10·0

(These values are calculated from the overall rate of reaction; subtraction of the neutral rates changes them insignificantly.) The actual numerical values have no particular significance, because the relative amounts of reactions $A_{Al}1$ and $A_{Ac}2$ are changing with temperature, acid concentration, and ionic strength.

The isotopic and the kinetic method both show that the extent of the unimolecular mechanism, $A_{Al}1$, increases relative to that of $A_{Ac}2$ with increasing temperature and perchloric acid concentration.

The rate of acid hydrolysis of diphenylmethyl trifluoroacetate in dioxan–water (70 : 30 v/v) (by mechanism $A_{Ac}2$) is very similar to that of diphenylmethyl formate, and much greater than that of the acetate.[10] The effect of the fluorine atom in decreasing the basicity of diphenylmethyl trifluoroacetate is therefore offset by an increased rate of decomposition of the conjugate acid.

Relative Rates of Hydrolyses.—Comparison of the relative rates of hydrolysis of methyl, phenyl, and diphenylmethyl trifluoroacetate is complicated by the fact that hydrolysis of diphenylmethyl trifluoroacetate in neutral and acid solution has extra reaction paths ($B_{Al}1$ and $A_{Al}1$) over those available to the other esters. We can, however, make qualitative comparison between the reactivities of these three esters by choosing conditions in which there is little alkyl–oxygen fission of diphenylmethyl trifluoroacetate, *i.e.*, low temperatures and low concentrations of acid. The numerical values which we quote depend upon the temperature, because the hydrolyses of these esters have different activation energies [1] (and p. 945 and above).

For hydrolysis in initially neutral dioxan–water (70 : 30 v/v) at 0°, the relative rates of mechanism $B_{Ac}2$ are: diphenylmethyl 1; methyl 10; phenyl, 2600. The relatively low reactivity of the diphenylmethyl ester may be caused by steric hindrance by the phenyl groups to the incoming water molecule. The hydrolyses in alkaline solutions of sodium carbonate or sodium hydrogen carbonate have (qualitatively) the same sequence of rates.

The rate constants for the acid hydrolysis of methyl and phenyl trifluoroacetate cannot be determined very accurately, because a small acid-catalysis is superimposed upon a neutral hydrolysis, and both are subject to negative salt effects. We compare the rates of acid hydrolysis at 0°, because at this temperature, and at a low acid concentration, the hydrolysis of all three esters should be by the same mechanism, $A_{Ac}2$. (The value for diphenylmethyl trifluoroacetate is calculated from rate constants at 25°, by using a value of E of 14 kcal. mole^{-1}; cf. above.)

The values of the second-order rate constants, $10^5 k_a$, in units of sec.$^{-1}$ mole^{-1} l., are: diphenylmethyl — (6); methyl 30 (47); phenyl, 2100. [The comparison is for the solvents dioxan–water (70 : 30 v/v), with values for the 60 : 40 mixture in parentheses.]

Where comparison is possible the rates are greater in the more aqueous solvent (see

[16] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372; Long, Pritchard, and Stafford, *ibid.*, 1957, **79**, 2362.

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also ref. 1 and Table 3), because in it the protonating power of the acid is greater.[17,18] The structural factors which affect the rate of a specific hydrogen-ion catalysed reaction are the basicity of the neutral molecule and the reactivity of the conjugate acid. The sequence of the basicities of the three esters is probably: methyl > diphenylmethyl > phenyl. This is not the sequence of the acid rates, and it seems that the ease of breakdown of the conjugate acid is the more important factor.

Comparison between the hydrolyses of diphenylmethyl formate, acetate, and trifluoroacetate shows that the powerful electron-attracting fluorine atoms facilitate both bimolecular attack upon the acyl-carbon atom, and unimolecular alkyl–oxygen bond fission;[19] there is, however, no striking enhancement of the latter relative to the former. The $B_{Ac}2$ mechanism is accelerated much more than the acid mechanisms $A_{Ac}2$ and $A_{Al}1$; *e.g.*, the hydrolysis of diphenylmethyl trifluoroacetate in alkaline solution is very rapid, whereas that of diphenylmethyl formate can be followed by acid–base titration;[10] the acid hydrolyses have similar rates (p. 949). To this extent the trifluoroacetates are similar to the esters of the tetra-alkylammonio-acetic acids, whose alkaline hydrolysis is very rapid and whose acid hydrolysis is slow relative to those of acetates.[20]

The kinetic forms for methyl and phenyl trifluoroacetate are very similar, *e.g.*, both show a levelling off, or a maximum, in the rate of hydrolysis in acid, at $[H^+]$ *ca.* 1·5M, which is not associated with complete protonation. So far as we know, the only other examples of this behaviour are the acid hydrolyses of some aryl phosphates.[21] In all these reactions the acyl–oxygen bond (or the equivalent bond in the phosphates) is broken. Diphenylmethyl trifluoroacetate, with appreciable alkyl–oxygen fission in acid solution, shows no such effects (Fig. 2).

Somewhat similarly, increase in ionic strength decreases the rates of neutral and acid hydrolysis of methyl [1] and phenyl trifluoroacetate, and increases those of diphenylmethyl trifluoroacetate (Tables 1 and 3).

Experimental

Materials.—Phenyl trifluoroacetate, prepared from phenol and trifluoroacetic anhydride,[22] and fractionated through a 30 cm. helix-packed column, had b. p. 149° and n_D^{25} 1·4247.

Diphenylmethyl trifluoroacetate was prepared by the reaction of diphenylmethanol (0·25 mole) with trifluoroacetic anhydride (0·25 mole) in sodium-dried ether. The solution was cooled and stirred vigorously. On the following day the volatile materials were removed *in vacuo*, and the ester was distilled under reduced pressure. Diphenylmethyl trifluoroacetate had b. p. 93°/2·5 mm., n_D^{25} 1·500 (Found: C, 63·6; H, 4·0%; equiv., 282. $C_{15}H_{11}F_3O_2$ requires C, 64·2; H, 3·9%; equiv., 280).

The solvent was aqueous dioxan as already described.[1]

Kinetic Measurements.—Phenyl trifluoroacetate. The solvent was dioxan–water (70 : 30 v/v). The reaction was followed by estimating the phenol produced,[23] by means of a stock solution of bromine (bromine 8 c.c., sodium acetate trihydrate 120 g., and acetic acid 100 c.c., made up to 1 l. with water). The concentration of sodium acetate was always sufficient to neutralise the acid present in the reaction solution, and that formed in the bromination, and for runs at high acid concentration extra sodium acetate was added.

Two procedures were used. (1) Samples (5 c.c.) of the reaction solution were added as rapidly as possible to a mixture (5 c.c.) of the bromine solution and carbon tetrachloride. The flask was shaken vigorously for 7 sec., and an excess of potassium iodide then added with shaking. This time of 7 sec. was sufficient for complete bromination, and no further reaction of phenol occurred after addition of the iodide. The carbon tetrachloride reduces the volatility

[17] Braude and Stern, *J.*, 1948, 1976.
[18] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.
[19] Cf. Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.
[20] Bell and Lindars, *J.*, 1954, 4601.
[21] Vernon, *Chem. Soc. Spec. Publ.*, 1957, No. 8, p. 17; unpublished results by Barnard, Silver, and Welch; Holbrook and Ouellet, *Canad. J. Chem.*, 1958, **36**, 698.
[22] Clark and Simons, *J. Amer. Chem. Soc.*, 1953, **75**, 6305.
[23] Waters, *J.*, 1936, 1014.

of bromine, and also stops the hydrolysis by extracting the ester from the aqueous phase. There is thus some uncertainty in time, depending upon the vigour of the shaking.

For this reason an alternative procedure (2) was used to test the method. Instead of carbon tetrachloride, purified dioxan (10 c.c.) was present during the bromination, which took place in homogeneous solution. Excess of potassium iodide was added 5 sec. after addition of the reaction solution. This method gave slightly higher results than the first (see Table 1 and Fig. 1), probably because hydrolysis continued during the 5 sec. before addition of the iodide.

The iodine liberated was titrated with 0·05N-sodium thiosulphate; no indicator was used. The copious precipitate formed during titrations, for runs catalysed by perchloric acid, did not appear to affect the results. An example of a kinetic run at 0° is given:

$[HClO_4]$ 0·54M, $[CF_3{\cdot}CO_2Ph]$ *ca.* 0·05M. Titration method 1.

Time (sec.)	36	63	90	116	142	165	∞
Titre (c.c.)	29·6	23·9	19·9	17·8	16·0	14·6	9·49, 9·42

10^3k_1 = 10·4 (sec.$^{-1}$), calc. graphically from the integrated first-order rate equation.

The alkaline hydrolysis, even with sodium hydrogen carbonate in dioxan–water (60 : 40 v/v) at 0°, was too fast for measurement by our methods.

Diphenylmethyl Trifluoroacetate.—Hydrolysis in initially neutral solution was followed titrimetrically by the method used for methyl trifluoroacetate.[1] The acid produced was estimated by the reaction:[24] $6H^+ + 5I^- + IO_3^- \longrightarrow 3I_2 + 3H_2O$.

Stoppered flasks were used at all temperatures except 45·2° (at which sealed tubes were used). Slight autocatalysis was observed in the neutral hydrolysis, as for the methyl ester; therefore initial values are quoted.

An example of a run in initially neutral dioxan–water (60 : 40 v/v) at 25° is given.

Ester *ca.* 0·03M. Concns. given in c.c. of 0·025N-sodium thiosulphate per 5 c.c. portion.

Time (min.)	4	30	60	92	120	150	203
[Ester]	5·85	5·15	4·20	3·40	2·75	2·25	1·50

10^5k_1 = 9·44 sec.$^{-1}$ (initial rate constant); at time = 200 min.
10^5k_1 = 15·3 sec.$^{-1}$. Both constants evaluated graphically, from the integrated first-order rate equation.

The intervention of azide ions was used as a test for carbonium-ion formation during neutral hydrolysis. The amount of acid produced after complete reaction was estimated by acid–base titration (phenolphthalein indicator); reactions in which sodium azide was present gave a milky emulsion, probably of diphenylmethyl azide. Most of these intervention experiments (Table 4) were made at the higher temperatures, because here carbonium-ion formation is of most importance. Unfortunately much reaction occurred while the solution was coming to thermostat temperature; *e.g.*, at 72·9° the half-life is *ca.* ½ min. These intervention experiments may therefore underestimate the extent of carbonium-ion formation.

The acid-catalysed reaction was followed dilatometrically, and the first-order rate constants were calculated by Guggenheim's method.[25] An example is given:

Solvent: dioxan–water (60 : 40 v/v). 25·0°. $[HClO_4]$ 0·365M.
[Ester] *ca.* 0·03M. Alternate points are quoted.

Time (min.)	10	20	30	40	50	60	70	80	90
h_t (mm.)	18·43	16·66	15·11	13·86	12·91	12·12	11·49	11·01	10·59
$h_{t+\tau}$ (min.)	10·29	9·89	9·81	9·62	9·43	9·35	9·28	9·18	9·10

10^5k_1 = 35·3 (sec.$^{-1}$), calculated graphically.

Alkaline hydrolysis with sodium hydroxide was too fast for measurement by conventional methods; we therefore followed the reaction with sodium hydrogen carbonate at 17°, in dioxan–water (60 : 40 v/v). With [Ester] = 0·032M, $[NaHCO_3]$ = 0·0415N, $t_{1/2} \approx 7$ min. The hydrolysis is therefore much slower than those of methyl [1] and phenyl trifluoroacetate.

The values for Hammett's acidity function for perchloric acid in aqueous dioxan have been reported earlier.[18]

Tracer Experiments.—Reactions were taken to completion in solvent with the water enriched in ^{18}O.

[24] Gorrin, Pierce, and McBee, *J. Amer. Chem. Soc.*, 1953, **75**, 5622.
[25] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

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Phenyl trifluoroacetate. The acid and neutral hydrolyses were made under kinetic conditions at 0°. After hydrolysis, the acid was neutralised with potassium hydroxide, any precipitate filtered off, the solution made slightly acid, and the phenol extracted with ether. The recrystallised phenol was dried over phosphoric oxide.

Neutral hydrolysis: Phenol, isotopic abundance 0·021 atom % excess, was isolated from hydrolysis with the abundance of water 0·595 atom % excess.

Acid hydrolysis: Phenol isolated had 0·017 and the water 0·385 atom % excess; hydrolysis was with $[HClO_4] = 2{\cdot}4$M. The alkaline hydrolysis was in aqueous 0·7M-sodium hydroxide at room temperature. After complete reaction the solution was acidified, and the phenol isolated as described. The abundances were phenol 0·016 and water 0·595 atom % excess.

Diphenylmethyl Trifluoroacetate.—Diphenylmethanol was isolated after the reaction was complete and purified by recrystallisation from light petroleum. For hydrolysis under neutral conditions an excess of 2,6-lutidine was added to the solvent; [11] it was assumed that this base would not affect the reaction. Control tests were made with diphenylmethanol in the isotopically enriched solvent containing 2,6-lutidine, and a correction applied.

The acid hydrolysis was made under kinetic conditions; control experiments were made on the exchange between diphenyl methanol and water, and a correction was applied.

The alkaline hydrolysis was made by shaking the ester with $H_2{}^{18}O$ containing 0·5M-sodium hydroxide.

Isotopic abundances of phenol and diphenylmethanol were determined by pyrolysis to carbon monoxide, over red-hot carbon *in vacuo*, and mass-spectrometric analysis of this gas. All the isotopic abundances were expressed in atom % excess above normal.

Appendix

Calculation of the Rate Constants for the Acid-catalysed Hydrolysis of Phenyl Trifluoroacetate.—Because the extent of acid-catalysis is small, and because of uncertainty in the initial slope of

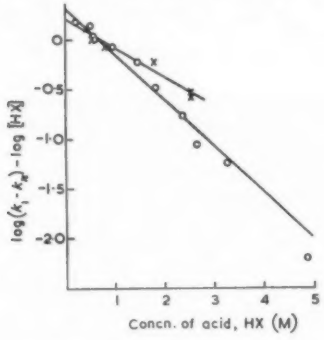

Fig. 3. *Calculation of rate constants for acid-catalysed hydrolysis of phenyl trifluoroacetate.*
○ *Perchloric acid.*
× *Toluene-*p*-sulphonic acid.*

Fig. 1, it is difficult to estimate k_a, the second-order rate constant for acid hydrolysis, where $\mu \longrightarrow 0$. The following extrapolation procedure was used. For ionic strengths (μ) outside the Debye–Hückel region the relation between rate (v) and ionic strength approximates to: [5]

$$v = v_0 \exp(-\beta\mu)$$

We assume that the salt effects upon the neutral rate of perchloric and toluene-*p*-sulphonic acid will be approximately the same as those of their lithium and sodium salts respectively; thus for the neutral hydrolysis in perchloric acid $\beta = 0{\cdot}19$, and for that in toluene-*p*-sulphonic acid $\beta = 0{\cdot}56$. Thus at any acidity we can estimate k_n, the first-order rate constant for the neutral hydrolysis. This value of k_n, subtracted from the overall first-order rate constant, k_1, gives the first-order rate for the acid hydrolysis. This will be related to k_n by

$$(k_1 - k_n) = k_a[HX] \exp(-\beta_x\mu)$$

or

$$\log(k_1 - k_n) - \log k_a - \log[HX] = -\beta_X\mu/2{\cdot}3$$

(and $\mu = [HX]$).

A plot of the acid concentration against {log ($k_1 - k_n$) − log [HX]} should be a straight line, and extrapolate to log k_a for [HX] = 0 (Fig. 3). The points for perchloric and toluene-*p*-sulphonic acid do not coincide, the slope being less for the latter. The calculated values of k_a are: perchloric acid $10^3k_a = 21$ (sec.$^{-1}$ mole^{-1} l.), and toluene-*p*-sulphonic acid $10^3k_a = ca.\ 16$ (sec.$^{-1}$ mole^{-1} l.), at 0°.

The most serious uncertainty in this calculation is the assumption that a strong acid and its salt have similar negative salt effects upon a reaction. This is not reasonable for high ionic strengths, if only because the acid will reduce the activity of the water more than does the salt; by an extrapolation to zero acid concentration we reduce the effect of this uncertainty.

We have applied this calculation to the acid hydrolysis of the methyl ester, and find reasonable agreement with our original values (in parentheses):

dioxan–water (60 : 40 v/v); $10^4k_a = 4{\cdot}6$ (sec.$^{-1}$ mole^{-1} l.) (4·7)
dioxan–water (40 : 60 v/v); $10^4k_a = 13$ (sec.$^{-1}$ mole^{-1} l.) (12·7)

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[*Received, August 11th*, 1960.]

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196. 4-*Nitro*-2,6-*di*-t-*butylphenol and its Thermal Decomposition.*

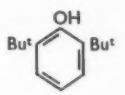
By T. J. BARNES and W. J. HICKINBOTTOM.

2,6-Di-t-butylphenol can be nitrated at position 4 in acetic acid solution by nitric acid. Other products are 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone and 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl with some 2,6-di-t-butyl-1,4-benzoquinone.

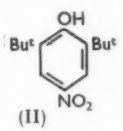
When heated, the nitrophenol decomposes into nitric oxide, 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone, 2,6-di-t-butyl-1,4-benzoquinone 4-oxime, and water.

Other reactions resulting in the elimination of the nitro-group of the nitrophenol are reported.

PREVIOUS attempts to nitrate 2,6-di-t-butylphenol (I) resulted either in oxidation to 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone [1] (III) or in the expulsion of a t-butyl-group with the formation of 2,4-dinitro-6-t-butylphenol.[2] It is now shown that, by attention to detail, mononitration of the phenol can be achieved; * the yield of 4-nitro-2,6-di-t-butylphenol (II) is about 30%, the remainder of the product being 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone (III) and 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl with some 2,6-di-t-butyl-1,4-benzoquinone.



(I)



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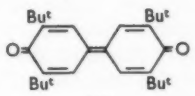

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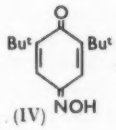

(IV)

The reactions of the nitrophenol (II) are unusual: it gives the Liebermann nitroso-test; it decomposes on being heated into the diphenoquinone (III), nitric oxide, and water; it is hydrolysed by sulphuric acid to 2,6-di-t-butyl-1,4-benzoquinone and its

* After this paper had been completed we learnt that Dr. K. U. Ingold has also prepared 4-nitro-2,6-di-t-butylphenol by nitration of 2,6-di-t-butylphenol, and that he has hydrogenated it to the aminophenol.

[1] (*a*) Kharasch and Joshi, *J. Org. Chem.*, 1957, **22**, 1439; (*b*) Bachman and Dever, *J. Amer. Chem. Soc.*, 1958, **80**, 5871.
[2] Hart and Cassis, *J. Amer. Chem. Soc.*, 1951, **73**, 3179.

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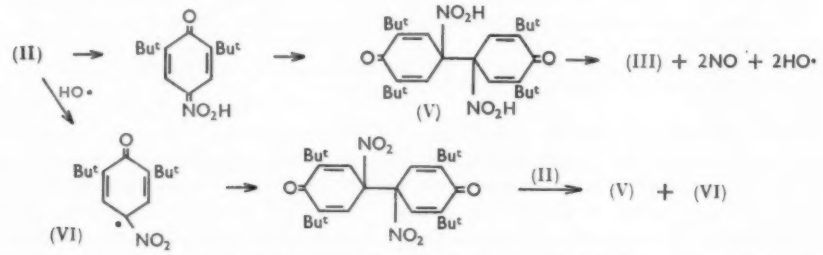
mono-oxime (IV), and is converted by zinc and acetic acid into 4,4'-dihydroxy-3,3',5,5'-tetra-t-butylbiphenyl.

Nevertheless, the evidence in support of its nitrophenol structure is conclusive. (*a*) It is hydrogenated to an aminophenol and this can be diazotised or oxidised (to 2,6-di-t-butyl-1,4-benzoquinone), and has been characterised by its *N*-acetyl derivative. The structure assigned to this acetyl compound is supported by infrared bands at 2·77 (free phenolic OH), 3·03, 6·47, 7·64 (secondary amido-group), 6·03 (>C=O), and 5·7 μ (aromatic nucleus having 1,2,3,5-substituents). (*b*) The infrared spectrum (potassium chloride disc) has strong bands at 6·62 and 7·55 (>C·NO_2), a sharp band at 2·80 (free OH), and a pattern of two bands in the 5·5 μ region consistent with two non-adjacent ring hydrogen atoms. (*c*) The hydrogen resonance spectrum (in carbon disulphide) has three bands with τ values of 8·54, 4·37, and 3·57, due to t-butyl, phenolic, and aromatic hydrogen respectively.

For comparison, 2,6-di-t-butyl-4-nitrosophenol was prepared by the action of nitrous acid on 2,6-di-t-butylphenol under conditions controlled to minimise oxidation. Oxidation of the nitrosophenol by alkaline ferricyanide gives the nitrophenol (II), in poor yield, with considerable amounts of diphenoquinone (III) and the monoquinone. The nitrophenol (II) is oxidised by hot alkaline ferricyanide to the diquinone (III).

The unusual reactions of the nitrophenol (II) may be ascribed to the presence of 2,6-substituents: a number of 2,6-disubstituted 4-nitrophenols decompose when heated.[3] The only serious investigation is by Jones and Kenner [3a] who established that nitric oxide is evolved when a number of 2,6-disubstituted 4-nitrophenols are heated alone or in acetic acid. The identification of the non-gaseous products of the decomposition was less satisfactory; a 2,6-disubstituted 1,4-benzoquinone was recognised as a product of the decomposition of some nitrophenols and it was suggested that a diphenoquinone was also formed from two of these.



In this paper it is shown that 4-nitro-2,6-di-t-butylphenol (II) decomposes thermally in dodecane to give nitric oxide, water, the diphenoquinone (III), and a small amount of the mono-oxime of 2,6-di-t-butyl-1,4-benzoquinone (IV). The formation of the diphenoquinone strongly suggests a free-radical mechanism and this view is supported by the behaviour of the nitrophenol (II) in acid solution: 2,6-di-t-butyl-1,4-benzoquinone and its mono-oxime are formed under these conditions. The above scheme based on a free-radical mechanism provides a satisfactory explanation of the course of the decomposition.

Experimental

Nitration of 2,6-Di-t-butylphenol.—A mixture of nitric acid (*d* 1·5; 4·71 g.) and acetic acid (15 c.c.) was added dropwise during 15 min. to a stirred solution of 2,6-di-t-butylphenol (15·45 g.) in acetic acid (100 c.c.) at 0—5°. A brown solid began to separate in the later stages of the nitration. The mixture was poured into an excess of water (1 l.) about 20 min. after all the nitric acid had been added, and the resulting suspension was made alkaline by the gradual

[3] (*a*) Armstrong and Brown, *Ber.*, 1874, **7**, 926; (*b*) Post, *Annalen*, 1880, **205**, 91; (*c*) Perkin and Mackenzie, *J.*, 1892, **61**, 869; (*d*) Fries and Oehmke, *Annalen*, 1928, **462**, 1; (*e*) Jones and Kenner, *J.*, 1931, 1842.

addition of solid sodium hydroxide. There remained undissolved a brown solid (A). The greenish-yellow aqueous alkaline solution (B) contained the nitrophenol (II).

2,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (III) was obtained from the solid (A) by crystallisation from alcohol. From the more soluble fractions of this crystallisation 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl (VII) and 2,6-di-t-butyl-1,4-benzoquinone were isolated by fractional precipitation with water and then further crystallisation.

The benzoquinone was isolated more conveniently by steam-distillation of material (A).

4-*Nitro*-2,6-*di*-t-*butylphenol* (II), precipitated from solution (B) by careful addition of an excess of hydrochloric acid, crystallises from alcohol or light petroleum (b. p. 100—120°) as pale yellow plates or needles, m. p. 157·5° (decomp.) (Found: C, 66·9; H, 8·2; N, 5·5. $C_{14}H_{21}NO_3$ requires C, 66·9; H, 8·4; N, 5·6%). The *α-naphthylurethane* was prepared by heating the compound at 100° with α-naphthyl isocyanate and a little pyridine; it had m. p. 200° (decomp.) (Found: C, 71·7; H, 6·6; N, 6·7. $C_{25}H_{28}N_2O_4$ requires C, 71·4; H, 6·7; N, 6·7%).

3,3,5,5-Tetra-t-butyl-4,4′-diphenoquinone, red needles (from alcohol), m. p. 246—247·5° (Hart and Cassis [2] give m. p. 245—247°) (Found: C, 82·1; H, 9·8. Calc. for $C_{28}H_{40}O_2$: C, 82·3; H, 9·9%), was identified by comparison (infrared and mixed m. p.) with a sample from another source. It is reduced by zinc dust in hot acetic acid to 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl, m. p. 185—185·5° (Kharasch and Joshi [1a] give m. p. 185°) (Found: C, 81·7; H, 10·25. Calc. for $C_{28}H_{42}O_2$: C, 81·9; H, 10·3%), identical (infrared and mixed m. p.) with that isolated directly after nitration of 2,6-di-t-butylphenol (Found: C, 82·2; H, 10·1%). This phenol is readily oxidised to the diphenoquinone, even when boiled with decolorising charcoal in alcohol.

2,6-Di-t-butyl-1,4-benzoquinone formed deep yellow needles (from aqueous alcohol), m. p. 66—67° (Metro [4] gives m. p. 65—66°) (Found: C, 76·2; H, 9·2. Calc. for $C_{14}H_{20}O_2$: C, 76·3; H, 9·15%) [2,4-dinitrophenylhydrazone, yellow needles (from alcohol), m. p. 201° (Metro [4] gives m. p. 198—200°)]. Yields from the nitration were: (II) 36, (III) 42, (VII) 20, and the benzoquinone 2%.

Reactions of 4-*Nitro*-2,6-*di*-t-*butylphenol.*—(a) *Various.* The nitrophenol in concentrated sulphuric acid gives a bright green solution which slowly becomes brown, with evolution of sulphur dioxide. From this brown solution, 2,6-di-t-butyl-1,4-benzoquinone oxime (IV) was isolated by dilution with water and extraction with ether. It was identified by its infrared spectrum and mixed m. p.

The nitrophenol (0·1 g.) was boiled in acetic acid (3 c.c.) containing aqueous (60%) sulphuric acid; 2,6-di-t-butyl-1,4-benzoquinone was then isolated by neutralisation with sodium carbonate and extraction with ether, forming yellow needles, m. p. and mixed m. p. 67° (yield 68%) (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 200·5°).

When the nitrophenol is heated in acetic acid with nitric acid (*d* 1·5) at 65—70° the solution becomes paler and nitrous fumes are evolved; picric acid, m. p. and mixed m. p. 122°, is formed.

The nitrophenol was recovered unchanged on acidification after its alkaline solution had been boiled for 10 min.

(b) *Reduction.* (i) Hydrogenation of the nitrophenol (2 g.) at 3½ atm. in ethyl acetate (150 c.c.) containing platinic oxide (0·3 g.) gave a colourless solution after 10 hr. On exposure to air, it changed through olive-green to red. A portion of this solution, evaporated to dryness, left a red tar out of which grew yellow needles during 2 months. These were identified as 2,6-di-t-butyl-1,4-benzoquinone (mixed, m. p. and infrared spectrum) (Found: C, 76·4; H, 9·25. Calc. for $C_{14}H_{20}O_2$: C, 76·3; H, 9·15%).

Another portion of the hydrogenated product, diluted with acetic acid, was added to nitrosylsulphuric acid in sulphuric acid. On treatment with alkaline β-naphthol a red-brown precipitate was obtained having the character of an azo-compound; it gave a purple colour with sulphuric acid, discharged by dilution with water.

The remainder of the hydrogenated solution (45 c.c.) was mixed with acetic anhydride (10 c.c.) and kept overnight. The dark tar resulting on evaporation was extracted with light petroleum (b. p. 60—80°), to give 4-*acetamido*-2,6-*di*-t-*butylphenol*, pale cream prisms, m. p. 170—170·5° (from aqueous alcohol) (Found: C, 72·75; H, 9·7; N, 5·4. $C_{16}H_{25}NO_3$ requires C, 73·0; H, 9·6; N, 5·3%).

[4] Metro, *J. Amer. Chem. Soc.*, 1955, **77**, 2901.

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(ii) The nitrophenol was also reduced when heated with an excess of cyclohexene and palladium–charcoal for 20 hr. under reflux.[5] The resulting aminophenol was identified by its *N*-acetyl derivative, m. p. and mixed m. p. 170·5°.

(iii) A solution of the nitrophenol (0·5 g.) in glacial acetic acid (15 c.c.) was refluxed for ½ hr. with zinc dust (0·1 g.). Nitrous fumes were evolved in the early stages and the colour, initially yellow, was rapidly discharged, then changed to red and again vanished. Dilution with water precipitated 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl (0·4 g.) (Found: C, 82·0; H, 10·15. Calc. for $C_{28}H_{42}O_2$: C, 81·9; H, 10·3%), identical with that obtained by nitration of 2,6-di-t-butylphenol (mixed m. p. and infrared spectrum).

(b) *Thermal decomposition.* (i) In acetic anhydride. The nitrophenol (1 g.) in pyridine (3 c.c.) and acetic anhydride (15 c.c.) was heated under reflux. Soon there was evolution of nitrous fumes and the solution became dark with the separation of red-brown crystals having a bluish-purple sheen; pale yellow crystals sublimed into the condenser. These solids were combined (0·85 g.) and separated by sublimation into 2,6-di-t-butyl-1,4-benzoquinone, m. p. and mixed m. p. 67° (0·6 g.), and the diphenoquinone (III), m. p. and mixed m. p. 245—246° (0·15 g.).

(ii) In dodecane. The nitrophenol (2·5 g.) in dodecane (50 c.c.) was heated for 3 hr. in a slow stream of nitrogen at 215°. Gas was evolved as the solution changed in colour from deep amber to deep ruby-red. The gas was condensed in a liquid-nitrogen trap to a blue solid and was identified as nitric oxide. The dodecane solution was evaporated under reduced pressure to yield 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone, m. p. and mixed m. p. 247° (1·3 g.). Extraction of the final oily residue with aqueous alkali gave an intensely yellow aqueous solution, which on acidification gave a mixture (0·15 g.) of unchanged nitrophenol (II) and 2,6-di-t-butyl-1,4-benzoquinone 4-oxime (IV) in about equal amounts (estimated by infrared absorption).

Preparation of 2,6-*Di*-t-*butyl*-1,4-*benzoquinone* 4-*Oxime* (IV).—Dilute hydrochloric acid was added gradually to a stirred suspension of sodium nitrite (0·7 g.) and powdered sodium hydroxide in an alcoholic solution of 2,6-di-t-butylphenol (2 g.) until a slight excess of acid was present. Dilution with water precipitated 2,6-di-t-butyl-1,4-benzoquinone 4-oxime that was isolated by means of ether and crystallised from chloroform–light petroleum (b. p. 60—80°) and then twice from ethyl alcohol as pale yellow plates, m. p. 225—226° (decomp.) (Found: C, 71·2; H, 9·0; N, 6·1%; *M*, 237. Calc. for $C_{14}H_{21}NO_2$: C, 71·45; H, 9·0; N, 5·9%; *M*, 235) (Metro [4] gives m. p. 219—220°).

This oxime is also obtained, less satisfactorily, by adding sodium nitrite to a solution of 2,6-di-t-butylphenol in acetic acid. There are also formed the diphenoquinone (III) and 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl.

The oxime gives a bright yellow solution in aqueous alkali from which it is precipitated unchanged on acidification. In sulphuric acid a yellow solution is formed changing to brown, with slight evolution of sulphur dioxide. The oxime was recovered unchanged when such a solution was diluted with water after 9 days.

Oxidation of an alkaline solution of the oxime by ferricyanide [6] gave the diphenoquinone (III) and the benzoquinone in about equal amounts. If the oxidation mixture is acidified immediately after the reactants have been mixed, a poor yield of 4-nitro-2,6-di-t-butylphenol (identified by its infrared spectrum) is obtained together with a large amount of the oxime.

The oxime is oxidised by boiling alkaline permanganate to the diphenoquinone and a relatively small proportion of the benzoquinone.

The authors thank the Hydrocarbons Research Group of the Institute of Petroleum for support. One of them (T.J.B.) is indebted to the Governors of Queen Mary College for the award of a Research Studentship. The authors also acknowledge gratefully the help they have received from the B.P. Research Centre, Sunbury, and from E.R.D.E., Waltham Abbey, in the interpretation of infrared spectra and hydrogen resonance spectra and for much useful discussion. Mr. P. D. Cook of this College was responsible for the infrared spectra.

Queen Mary College (University of London), London, E.1. [*Received, August 15th*, 1960.]

[5] Braude, Linstead, and Wooldridge, *J.*, 1954, 3590.
[6] Borsche and Berkhout, *Annalen*, 1904, **330**, 95.

197. *Hydrogen Bonding in Some Thiosemicarbazones and Thioamides.*

By P. W. Sadler.

The infrared spectra of some heterocyclic thioamides and *S*- and *N*-methylthiosemicarbazones indicate that intermolecular N–H · · · N hydrogen bonds may be formed in addition to N–H · · · S bonds. Both the 2- and 4-imino-groups of thiosemicarbazones may be involved. In α-diketone monothiosemicarbazones strong intramolecular N–H · · · O=C bonds predominate; similar six-membered hydrogen-bonded rings occur in hydrazones and phenylhydrazones. No evidence was found, for any of the compounds, of tautomerism of the thione–thiol type, or for σ–ν correlations in a series of substituted isatin 3-thiosemicarbazones.

Many studies have been published of the infrared spectra of amides, but few of thioamides or thiosemicarbazones. Davison and Christie [1] recorded the infrared spectra of twenty-four semicarbazones of common ketones and aldehydes, as potassium chloride discs. They assigned characteristic absorptions at 3460 and 3370—2800 cm.$^{-1}$ to unbonded and bonded stretching modes. Strong absorptions at 1695 and 1585 cm.$^{-1}$ were assigned to the amide I and II bands, and a rather variable absorption at 1665 cm.$^{-1}$ was very tentatively assigned to a C=N stretching mode. Bogomolow, Postovskii, and Sheinker [2] reported similar bands for the semicarbazones of acetaldehyde and benzaldehyde and a band at 1516~1533 cm.$^{-1}$, which was found in the spectra of five simple thiosemicarbazones,

Table 1. *Frequencies (cm.$^{-1}$) for thioamides and thiosemicarbazones in potassium bromide discs.*

2-Thiopropionylbenzimidazole		3230	3040		1613		1472	1456	1380	1280	1242	877	
Indole-5-thiocarbonamide	3360	3260	3130		1612		1461	1431	1408	1288	1251	853	
3-Formylindole thiosemicarbazone		3200br			1611	1541		1444	1371	1297	1253	878	
Acetaldehyde thiosemicarbazone	3360	3250	3140		1596	1512	1460	1433	1366	1271	1250	867	
Benzaldehyde thiosemicarbazone	3400	3240	3130	2960	1591	1540	1470	1451	1375	1299	1230	870	
Benzaldehyde 4,4′-dimethylthiosemicarbazone	3400	3200			1595	1540		1440	1378	1299		876	
Benzaldehyde *S*-methylthiosemicarbazone	3400	3200			1600	1530		1440		1280		868	690

was assigned to a C=S stretching mode. The C=S vibration had been assigned by Thompson *et al.*[3] and Colthup [4] to the range 1300—1400 cm.$^{-1}$, and to 1410—1550 cm.$^{-1}$ by Miller; [5] but for thioamides the assignment has ranged from 1533 to 965 cm.$^{-1}$. Tentative assignments include bands at 1265—1180 cm.$^{-1}$ for thiopropionamide and *N*-butylthioacetamide [6] and 965 and 980 cm.$^{-1}$ for thiuram monosulphide and thioacetamide respectively.[7] Other assignments [8,9] for the C=S absorption in thioacetamide and thioformamide have favoured the range 1430—1300 cm.$^{-1}$. Our results (Table 1) include strong absorption at 1366—1408 cm.$^{-1}$ which is absent from the spectrum of benzaldehyde *S*-methylthiosemicarbazone, and this is tentatively assigned to a C=S stretching mode. The

[1] Davison and Christie, *J.*, 1955, 3389.
[2] Bogomolov, Postovskii, and Sheinker, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 1111.
[3] Thompson, Nicholson, and Short, *Discuss. Faraday Soc.*, 1950, **9**, 222.
[4] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[5] Miller, "Applications of Infrared and Ultraviolet Spectra to Organic Chemistry," in Gilman's "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, 1953, p. 149.
[6] Marvel, Radzitsky, and Brader, *J. Amer. Chem. Soc.*, 1955, **77**, 5997.
[7] Bellamy, *J.*, 1960, 2218.
[8] Mecke and Speisecke, *Chem. Ber.*, 1956, **89**, 1110.
[9] Davies and Jones, *J.*, 1958, 955.

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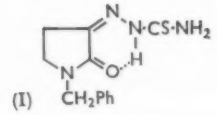
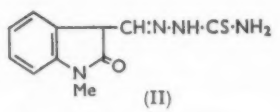
methyl derivative also has a strong band at 690 cm.$^{-1}$ which is within the range 685—705 cm.$^{-1}$ reported for an S–CH_3 stretching vibration.[10]

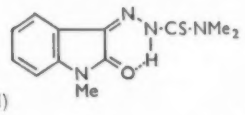
The 1512—1540 cm.$^{-1}$ band could be assigned to an N–H bending mode, in which case the 2′-imino-group must be mainly involved as neither the position nor the intensity of this band varies in benzaldehyde thiosemicarbazone and 4,4′-dimethylthiosemicarbazone. Strong absorption at 1590~1610 cm.$^{-1}$ is usually associated with a ring vibration, but the C=N group could also be responsible for it as conjugated systems containing both C=N and C=C linkages often exhibit one or more moderately strong bands between 1700 and 1500 cm.$^{-1}$. It is usually not possible to identify such bands with particular C=C or C=N linkages, but in this instance it appears to be primarily associated with the C=N group as the acetaldehyde derivative also shows a strong band at 1596 cm.$^{-1}$; this is about 30 cm.$^{-1}$ lower than the usual range quoted, but no other strong absorption is observed in this region. Somewhat similar results have been observed for a series of aliphatic aldehyde dimethylhydrazones, all of which show a peak in the 1610 cm.$^{-1}$ region attributable to the C=N stretching vibration. For dimethylhydrazones of aromatic and heterocyclic aldehydes interaction with the C=C group obscures this band, and two characteristic absorption bands, at 1613—1587 and 1580—1555 cm.$^{-1}$, result.[11] The two bands centred on 1280 and 1230 cm.$^{-1}$ (Table 1) may fairly confidently be assigned to C–N stretching vibration.



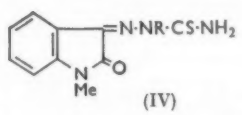
(I)



(II)



(III)



(IV)

The thiol group in a tautomer should display the thiol band at 2500 cm.$^{-1}$, but no bands are present in the 2500—2650 cm.$^{-1}$ region, so tautomerism of the thione–thiol type does not occur in these derivatives. This is in agreement with the observation by Hadži that each compound in a series of 4-arylthiosemicarbazones of α-keto-acids and the derived 2,3,4,5-tetrahydro-5-oxo-3-thiono-1,2,4-triazines exists in the thiono-form.[12]

Characteristic strong hydrogen bonds of the type normally encountered in amides are indicated for these compounds by the solid-state spectra in Table 1. Three strong N–H stretching frequencies are at 3400—3360, 3250—3200, and 3140—3040 cm.$^{-1}$; in most instances the C–H stretching frequency is merged with the lower N–H stretching frequency. Either the 2′- or the 4′-imino-hydrogen atom may be involved as benzaldehyde 4,4′-dimethylthiosemicarbazone and *S*-methylthiosemicarbazone have similar bonded N–H stretching frequencies. Amide-hydrogen bonding is usually of the intermolecular N–H···O=C type, with dimer or trimer formation, and similar structures may exist in thioamides. An accurate determination of the crystal structure of thioacetamide has shown that it consists of planar molecules which are probably held by N–H···S hydrogen bonds.[13] However, for the thiosemicarbazones listed in Table 2, several types of hydrogen bonding are possible owing to the presence of a carbonyl group adjacent to the C=N linkage; and as N–H···O=C bonds are stronger than N–H···N or N–H···S, the first type is likely to predominate. 1-Benzylpyrrolidine-2,3-dione 3-thiosemicarbazone (I) shows typical bonded N–H frequencies at 3360, 3240, and 3140 cm.$^{-1}$ due to the strong

[10] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.
[11] Wiley, Slaymaker, and Krauss, *J. Org. Chem.*, 1957, **22**, 204.
[12] Tišler and Urbaški, *J. Org. Chem.*, 1960, **25**, 770.
[13] Truter, *J.*, 1960, 997

intramolecular bond. 3-Formyl-1-methyloxindole thiosemicarbazone (II) shows similar N–H stretching frequencies, which probably result from intermolecular bonds (insolubility excludes solution spectra). The position of the carbonyl absorption in this compound is of particular interest. 1-Methyloxindole gives a single strong peak at 1700 cm.$^{-1}$ in chloroform, whereas for 3-formyl-1-methyloxindole the carbonyl peak is lowered to 1680 cm.$^{-1}$ owing to formation of a very strong intramolecular hydrogen bond, as indicated by a bonded O–H absorption appearing as a broad band between 2600 and 2400 cm.$^{-1}$. Therefore, the strong absorption at 1665 cm.$^{-1}$ in (II) represents the formation of much stronger hydrogen bonds than those in either 3-formyl-1-methyloxindole or its oxime, in which the carbonyl frequency lies at 1696 cm.$^{-1}$.

The 3-hydrazone, 3-phenylhydrazone, 3-thiosemicarbazone, and 3-4′-phenylthiosemicarbazone of 1-methylisatin all show bonded N–H frequencies at 3400 and 3200 cm.$^{-1}$ (Table 3). The broad band at 3400—3200 cm.$^{-1}$ shown by 1-methylisatin 3-4′,4′-dimethylthiosemicarbazone favours the intramolecular structure (III), which is supported by the data for the 2′-methyl and the 2′-phenyl derivative (IV; R = Me, Ph). Although these compounds in the solid state show bonded N–H frequencies the carbonyl stretching frequency of the 2′-phenyl derivative is raised to 1712 cm.$^{-1}$, and a similar peak appears as a shoulder at 1710 cm.$^{-1}$ in the 2′-methyl derivative. Compounds of type (IV) are unlikely to possess intramolecular hydrogen bonds and the intermolecular bonding

TABLE 2. *Frequencies (cm.$^{-1}$) for thiosemicarbazones and hydrazones of heterocyclic α-diketones in potassium bromide discs.*

1-Benzylpyrrolidine-2,3-dione 3-thiosemicarbazone	3360	3240	3140	1689	1611	1488	—	1359	—	1107	1076
3-Formyl-1-methyloxindole thiosemicarbazone	3340	3240	3160	1665	1607	1492	1470	1370	1347	1121	1098
1-Methylisatin 3-4′-phenylthiosemicarbazone	—	3200br	—	1677	1609	1493	1470	1368	1335	1158	1090
1-Methylisatin 3-hydrazone	3360	3200	—	1680	—	1493	1472	1376	1332	1115	1098
1-Methylisatin 3-phenylhydrazone	3400	3200	3160	1680	—	1510	1476	1376	1340	1120	1100
1-Methylisatin 3-2′-phenylthiosemicarbazone	3400	3200	2900	1712	1610	1489	1468	1374	1340	1152	1092
1-Methylisatin 3-2′-methylthiosemicarbazone	3400	3300	1710sh	1680	1610	1490	1470	1365	1320	1125	1100
1-Methylisatin 3-4′,4′-dimethylthiosemicarbazone	3400	3200	2960	1690	1615	—	1475	1375	1340	1120	1100

TABLE 3. *Frequencies (cm.$^{-1}$) for substituted isatin 3-thiosemicarbazones in potassium bromide discs.*

Subst.															
7-CF_3		3300	3200	1700	1625	1485	1330	1300		1110	1060	888	875	804	750
7-Br	3440	3270	3200	1690	1615	1475	1330	1285		1130	1060	884	852	794	728
5-F	3450	3290	3220	1680	1608	1485		1300		1135	1050	902	860	799	762
5-CH_2·CO_2Et	3420	3300	3200	1690	1620	1487		1270		1125	—	—	854	804	762
5-CH_2·CO_2H	3440	3300	3200	1680	1610	1480	1379	1276		1124	1057	897	863	809	758
—	3400	3230	3170	1685	1612	1485	1340	1270/80		1130	1055	884	850	788	750
5-Me	3400	3250		1680	1600	1480		1288		1127	1058	897	855	788	759
6-MeO	3425br		—	1680	1620/1580	1492		1305/1280		1120			856		756
1-Me	3410	3280	—	1685	1600	1485/70	1370	1340	1270	1100	1040	890		788	753
1-Me-4-CF_3	3450	3270	3190	1675	1600	1475	1360	1340	1300	1110	1065	907	837	780	
1-Me-5-CH_2·CO_2H	3420	3350		1675	1620	1475	1360	1339	1279	1101		908	852	783	738
1-Me-5-CH_2·CO_2Et	3410	3280	2920	1675	1600	1475	1360	1335	1270	1098	1032	904	842	787	740

appears to be rather weak. This is confirmed by results for dilute solutions in carbon tetrachloride. The compounds are not sufficiently soluble to provide good records in the 3 μ region, but 1-methylisatin 3-2′-phenyl- and 3-2′-methyl-thiosemicarbazone have peaks at 1722 and 1708 cm.$^{-1}$, respectively; whereas, 1-methylisatin 3-phenylhydrazone and compound (III) absorb strongly at 1687 and 1683 cm.$^{-1}$. Again, as in the case of oxindole,

the α-carbonyl stretching frequency is considerably lower for the 3-thiosemicarbazone than for the parent compound [14] or the 3-oxime.[15] The demonstration that strong intramolecular hydrogen bonds are formed in compounds of type (III) is important in interpreting the antivaccinial [16] and antivariola activities [17] of 1-alkylisatin 3-thiosemicarbazones.

Table 3 contains solid state spectroscopic data for some ring-substituted and *N*-methylated isatin 3-thiosemicarbazones. Correlation exists between σ-values of substituents [18] and both the α- and β-carbonyl stretching frequencies of substituted isatins,[14] and the latter frequencies are also directly related to the dehydrogenase activities of these compounds.[19] However, reference to Table 3 shows no sign of correlation between σ-values and either the α-carbonyl or C=N stretching frequency, in accord with the lack of relation of antivaccinial activities to σ-values of substituted isatin 3-thiosemicarbazones.[16]

Experimental.—Infrared absorption spectra. Spectra were determined by using a Perkin-Elmer 21 double-beam recording spectrometer fitted with a rock-salt prism. Preparative details for the compounds have already been given.[16]

The author thanks the D.S.I.R. for provision of a special research grant which has defrayed some of the cost of this work.

THE MIDDLESEX HOSPITAL, LONDON, W.1. [*Received, August 16th*, 1960.]

[14] O'Sullivan and Sadler, *J.*, 1956, 2202.
[15] O'Sullivan and Sadler, *J. Org. Chem.*, 1957, **22**, 283.
[16] Bauer and Sadler, *Brit. J. Pharmacol.*, 1960, **15**, 101.
[17] Bauer and Sadler, *Lancet*, 1960, **1**, 1110.
[18] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188.
[19] O'Sullivan and Sadler, *Arch. Biochem. Biophys.*, 1957, **66**, 243.

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198. *Some Potential Intermediates for the Synthesis of Diterpenes.*

By F. E. KING, T. J. KING, and G. READ.

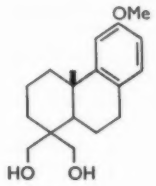
Syntheses of derivatives of the *gem*-di(hydroxymethyl)cyclohexene (IVb; R′ = H), the *gem*-di(hydroxymethyl)cyclohexanol (IIIb; R′ = R″ = H), and related compound are described.

THE diol (I) is a potential intermediate in the stereospecific synthesis of podocarpic acid, for it has been shown that the equatorial 1-hydroxymethyl group in vinhaticol can be converted into methyl by reduction of the toluenesulphonate ester whereas the corresponding axial group in vouacapenol cannot.[1] This paper describes the synthesis of several compounds containing the protected *gem*-di(hydroxymethyl) group, which, it was hoped, would cyclise to derivatives of the diol (I).

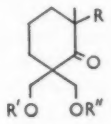
The tri(hydroxymethyl) ketone (II; R = CH_2·OH, R′ = R″ = H) was formed from 2-methylcyclohexanone by an aldol condensation with formaldehyde. It was obtained as a viscous, water-soluble oil and was characterised as its triacetate. The benzylidene derivative (II; R = CH_2·OH, R′ + R″ = C_6H_5·CH⟨) could not be isolated on reaction of the triol with benzaldehyde and hydrogen chloride, but treatment of the product with alkaline hydrogen peroxide afforded the ketone (II; R = H, R′ + R″ = C_6H_5·CH⟨). This crystalline compound melted sharply and gave a single peak on gas–liquid chromatography; it was therefore considered not to be a mixture of the two possible geometric isomers. The ketone (II; R = H, R′ + R″ = C_6H_5·CH⟨) condensed readily with lithium *p*-methoxyphenylacetylide to give the acetylenic carbinol (IIIa; R′ + R″ = C_6H_5·CH⟨)

[1] King, King, and Godson, *J.*, 1955, 1117.

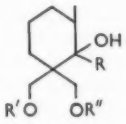
in which the hydroxyl (at $C_{(1)}$) and hydrogen (at $C_{(6)}$) appeared to be in *trans*-relationship since the alcohol readily lost water in addition to benzaldehyde on acid-hydrolysis, yielding the acetylenic diol (IVa; R′ = H). This compound and its diacetate (IVa; R′ = Ac) and ditoluene-*p*-sulphonate were reduced with hydrogen in the presence of palladised



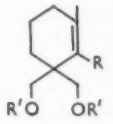
(I)



(II)



(III)



(IV)

a: R = ·C:C·C_6H_4·OMe
b: R = ·CH_2·CH_2·C_6H_4·OMe
c: R = ·CH:CH·C_6H_4·OMe

strontium carbonate to the respective cyclohexenes (IVb); the reductions proceeded stepwise and in the cases of the diol and the ditoluene-*p*-sulphonate the dienes (IVc) were isolated. The *cis*-ethylenic linkages in these products prevented coplanarity of the cyclohexene rings and their styryl substituents and their ultraviolet spectra resembled that of styrene.

Reduction of the acetylenic carbinol (IIIa; R′ + R″ = C_6H_5·CH⟨) with an aged sample of palladium black gave the cyclohexanol (IIIb; R′ + R″ = C_6H_5·CH⟨), whilst reduction with freshly prepared catalyst, under slightly acidic conditions, yielded the triol (IIIb; R′ = R″ = H) characterised as its diacetate. An attempt to convert this triol into its dibenzyl ether was not successful.

The diol (IVb; R′ = H), its diacetate and ditoluene-*p*-sulphonate, and the benzylidene compound (IIIb; R′ + R″ = C_6H_5·CH⟨) were subjected to a variety of cyclisation conditions. In no case was the desired derivative of the octahydrophenanthrene diol (I) obtained. The principal products appeared to be either polymers or monomers in which one or both protecting groups had been lost and water eliminated in accompanying Wagner–Meerwein rearrangements.

Experimental

The light petroleum used had b. p. 60—80°. Ultraviolet absorption spectra were determined in ethanol unless otherwise stated, on a Unicam S.P. 500 spectrophotometer.

2,2,6-*Tri*(*hydroxymethyl*)-6-*methylcyclohexanone*.—A 10% solution of formaldehyde (270 ml.) was added during 2 hr. to a stirred suspension of calcium hydroxide (15 g.) in a solution of 2-methylcyclohexanone (33·6 g.), dioxan (250 ml.), and water (900 ml.) at 0°. After a further 2 hr., the solution was filtered through a coarse filter paper, acidified with formic acid, and evaporated under reduced pressure at 45°, to give the crude product and calcium formate. The viscous mass was triturated with methanol (150 ml.) and filtered. Evaporation of the filtrate gave the crude triol (II; R = CH_2·OH, R′ = R″ = H) as a clear viscous involatile oil, soluble in all common solvents with the exception of benzene and light petroleum. Acetic anhydride–pyridine at 100° gave the *triacetate* (II; R = CH_2·OAc, R′ = R″ = Ac), b. p. 144—150° (bath)/0·3 mm. (Found: C, 58·8; H, 7·3; Ac, 36·6. $C_{16}H_{24}O_7$ requires C, 58·5; H, 7·4; Ac, 39·3%).

OO-*Benzylidene Derivative of* 2,2-*Di*(*hydroxymethylene*)-6-*methylcyclohexanone*.—Hydrogen chloride was bubbled through a solution of the crude triol (56 g.) in benzaldehyde (50 g.) maintained at −5°, until turbidity persisted. The reactants were shaken for 30 min. at room temperature, cooled to −5°, rapidly rendered alkaline to phenolphthalein by addition of a 5% ethanolic solution of sodium ethoxide (*ca.* 150 ml.), and diluted with water (400 ml.). The crude product obtained was extracted into ether, washed with 20% sodium hydrogen sulphite solution,

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sodium hydrogen carbonate solution, and water, and transferred to ethanol (180 ml.). 100-Vol. hydrogen peroxide (75 ml.) was added to this solution at 0° with stirring, followed by chilled 30% ethanolic potassium hydroxide solution (150 ml.), during 15 min. Further 100-vol. hydrogen peroxide (25 ml.) was added after 5 hr. and the solution allowed to attain room temperature overnight, efficient stirring being maintained. The resulting solution was diluted with water (800 ml.) and adjusted to about pH 8 with 6N-hydrochloric acid. Distillation of the product, isolated by ether-extraction, gave the crude *benzylidene ketone* (II; R = H, R′ + R″ = C_6H_5·CH<), b. p. 125—170°/0·08 mm. Crystallisations from ethanol afforded prisms, m. p. 102—103° (Found: C, 73·9; H, 7·5. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·8%). The yield was 18·2% based on 2-methylcyclohexanone. The ketone gave an *oxime*, needles (from aqueous methanol), m. p. 170—171° (Found: C, 70·4; H, 7·6; N, 5·05. $C_{16}H_{21}NO_3$ requires C, 69·9; H, 7·6; N, 5·1%), and a *semicarbazone*, prisms (from methanol), m. p. 215—216° (Found: C, 64·4; H, 7·4. $C_{17}H_{23}N_3O_3$ requires C, 64·3; H, 7·3%).

OO-*Benzylidene Derivative of* 2,2-*Di*(*hydroxymethyl*)-1-p-*methoxyphenylethynyl*-6-*methylcyclohexanol*.—The above ketone (6·2 g.) was added under nitrogen, batchwise during 15 min., to a stirred solution of lithium *p*-methoxyphenylacetylide in ether, prepared by adding *p*-methoxyphenylacetylene [2] (3·4 g.) in dry ether (10 ml.) to n-butyl-lithium [3] (1·5 g.) in dry ether (360 ml.) and refluxing the mixture for 2 hr. The solution was refluxed for 1·5 hr., then poured into chilled water. The crude product, obtained as a glass from the ethereal layer and ether-extracts of the aqueous phase, crystallised from light petroleum. Purification on an alumina column gave the *alcohol* (IIIa; R′ + R″ = C_6H_5·CH<) (7·3 g.) as prisms, m. p. 129—130° (Found: C, 76·5; H, 7·1. $C_{25}H_{28}O_4$ requires C, 76·5; H, 7·2%), $\lambda_{max.}$ 204 (log ε 4·82) and 253 mμ (log ε 4·44).

3,3-*Di*(*hydroxymethyl*)-2-p-*methoxyphenylethynyl*-1-*methylcyclohexene*.—A solution of the above alcohol (IIIa) (2 g.) in ethanol (200 ml.), containing concentrated sulphuric acid (2 ml.), was refluxed for 15 min., cooled, neutralised with solid sodium hydrogen carbonate, diluted with water, and extracted with ether. From the ether extract (150 ml.), washed with 10% sodium hydrogen sulphite solution (3 × 25 ml.) to remove benzaldehyde, was obtained the acetylenic *diol* (IVa; R′ = H) (1·3 g.), elongated prisms (from aqueous methanol), m. p. 98—99·5° (Found: C, 75·1; H, 7·7. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7%), $\lambda_{max.}$ 285 (log ε 4·40) and 301 mμ (log ε 4·27). The *diacetate*, prepared with acetic anhydride in pyridine at 100°, crystallised as needles (from aqueous methanol), m. p. 112—113° (Found: C, 71·3; H, 7·1. $C_{22}H_{26}O_5$ requires C, 71·3; H, 7·1%). The *ditoluene*-p-*sulphonate* was obtained, by treatment with toluene-*p*-sulphonyl chloride in pyridine at room temperature for 14 hr., as prisms (from ethanol), m. p. 123—124° (decomp.) or 136—137° (decomp.) on rapid heating (Found: C, 64·5; H, 5·6; S, 10·1. $C_{32}H_{34}O_7S_2$ requires C, 64·6; H, 5·8; S, 10·8%).

Reductions of 3,3-*Di*(*hydroxymethyl*)-2-p-*methoxyphenylethynyl*-1-*methylcyclohexene and its Derivatives*.—The acetylenic diol (IVa; R′ = H) (3·0 g.) was reduced in ethanol with hydrogen and 5% palladised strontium carbonate. Reduction ceased after an uptake of 2·1 mol. of hydrogen, and the diol (IVb; R′ = H) was obtained as an oil. Treatment with acetic anhydride–pyridine afforded 3,3-*di*(*acetoxymethyl*)-2-p-*methoxyphenethyl*-1-*methylcyclohexene* (IVb; R′ = Ac) (2·5 g.) as elongated prisms (from light petroleum), m. p. 63·5—64° (Found: C, 70·4; H, 8·1; Ac, 26·9. $C_{22}H_{30}O_5$ requires C, 70·6; H, 8·1; Ac, 27·3%).

By stopping a similar reduction when the hydrogen uptake had reached 1·2 mol., 3,3-*di*(*hydroxymethyl*)-2-2′-p-*methoxyphenylvinyl*-1-*methylcyclohexene* (IVc; R′ = H) was obtained as flat elongated prisms (from light petroleum), m. p. 106—107° (Found: C, 74·8; H, 8·8. $C_{18}H_{24}O_3$ requires C, 75·0; H, 8·4%), $\lambda_{max.}$ 205 (log ε 4·36) and 268 mμ (log ε 4·19).

Reduction of the acetylenic diacetate (IVa; R′ = Ac) under the same conditions gave the diacetate (IVb; R′ = Ac), m. p. and mixed m. p. 63—64°.

Reduction of the acetylenic ditoluene-*p*-sulphonate (1 g.) in ethyl acetate with 5% palladised strontium carbonate afforded the *diester* (IVb; R′ = *p*-$C_{10}H_4Me$·SO_2) (0·9 g.) as prisms (from acetone–light petroleum), m. p. 85—85·5° (decomp.) (Found: C, 63·9; H, 6·6; S, 10·3. $C_{32}H_{32}O_7S_2$ requires C, 64·2; H, 6·4; S, 10·7%).

A similar reduction was stopped after 1·1 mol. of hydrogen has been adsorbed and the *diene ditoluene*-p-*sulphonate* (IVc; R′ = C_6H_4Me·SO_2) was obtained as elongated prisms (from aqueous alcohol), m. p. 83—83·5° (decomp.), depressed to 79—79·5° (decomp.) when mixed with

[2] Bergmann and Bondi, *Ber.*, 1933, **66**, 278.
[3] Gilman, Bell, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949. **71**. 1499.

the toluene-*p*-sulphonate (IVb; R′ = $C_6H_4Me{\cdot}SO_2$) (Found: C, 64·3; H, 6·2; S, 10·2. $C_{32}H_{36}O_7S_2$ requires C, 64·4; H, 6·1; S, 10·7%), $\lambda_{max.}$ (in CH_2Cl_2) 267 mμ (log ε 4·17).

Reductions of the OO-*Benzylidene Derivative of* 2,2-*Di*(*hydroxymethyl*)-1-p-*methoxyphenylethynyl*-6-*methylcyclohexanol.*—(*a*) The acetylenic carbinol (IIIa; R′ + R″ = $C_6H_5{\cdot}CH$<) (4 g.) was hydrogenated in ethanol (30 ml.) containing concentrated hydrochloric acid (1 drop) over freshly prepared palladium black. Reduction ceased after 4·1 mol. of hydrogen had been adsorbed and the triol (IIIb; R′ = R″ = H) (2·9 g.) was obtained as an oil on filtration and removal of the solvent and toluene under reduced pressure. Treatment with acetic anhydride–pyridine at 100° gave 2,2-*di*(*acetoxymethyl*)-1-2′-p-*methoxyphenylethyl*-6-*methylcyclohexanol* (IIIb; R′ = R″ = Ac), b. p. 210° (bath)/0·04 mm. (Found: C, 67·3; H, 8·1; Ac, 23·6. $C_{22}H_{32}O_6$ requires C, 67·3; H, 8·2; Ac, 21·9%).

The triol, when kept in dry acetone over potassium carbonate for 3 days, was converted into the *isopropylidene derivative* (1·15 g.), b. p. 180—184° (bath)/0·03 mm. (Found: C, 72·3; H, 9·0. $C_{21}H_{32}O_4$ requires C, 72·4; H, 9·3%), which gave acetone on acid hydrolysis.

(*b*) The acetylenic carbinol (IIIa; R′ + R″ = $C_6H_5{\cdot}CH$<) (3 g.) in alcohol was reduced with an aged sample of palladium black. Reduction ceased after 1·8 mol. of hydrogen had been absorbed. Filtration and removal of the solvent gave the *benzylidene derivative* (IIIb; R′ + R″ = $C_6H_5{\cdot}CH$<) (2·5 g.) as an oil, b. p. 260° (bath)/0·01 mm. (Found: C, 76·1; H, 8·3. $C_{25}H_{32}O_4$ requires C, 75·7; H, 8·1%), which was hydrolysed with acid to give benzaldehyde.

The authors thank the Department of Scientific and Industrial Research for a Maintenance Allowance (to G. R.).

THE UNIVERSITY, NOTTINGHAM. [*Received, September 26th,* 1960.]

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199. *Uric Acid Riboside.* Part I. Isolation and Reinvestigation of the Structure.*

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Crystalline uric acid riboside has been isolated from beef blood, and its properties have been compared with those of 3-, 7-, and 9-methyluric acid. It is concluded that the compound is actually uric acid-3 riboside and not uric acid-9-riboside.

BETWEEN 1933 and 1939, Gulland and his co-workers compared the ultraviolet absorption spectra of the naturally occurring purine ribosides and deoxyribosides [1] with those of model compounds and concluded that in all cases the ribosyl or deoxyribosyl moiety was attached to the 9-position of the purine ring. For most of these compounds, the position of attachment has been confirmed by synthetic and/or other evidence. One of the compounds examined by Falconer and Gulland [1] was uric acid riboside which was obtained from beef blood and beef liver by a modification of the method of Davis, Newton, and Benedict.[2] The ultraviolet absorption spectrum of this compound, when compared with those of 1-, 3-, 7-, and 9-methyluric acid, closely resembled that of 9-methyluric acid, and it was concluded that the ribosyl group in this compound, as in the other naturally occurring ribosides, was attached to the 9-position. However, there has been no independent confirmation of the structure of uric acid riboside.

In a note appearing in 1952, Carter and Potter [3] reported the isolation from beef blood

* To avoid further confusion, the name uric acid riboside has been retained and used throughout this paper; ribosyluric acid is, however, the preferred name, and uric acid ribonucleoside could also be used. H. S. F.

[1] Falconer and Gulland, *J.*, 1939, 1369.
[2] Davis, Newton, and Benedict, *J. Biol. Chem.*, 1922, **54**, 595.
[3] Carter and Potter, *Fed. Proc.*, 1952, **11**, 195.

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of a uric acid riboside by a simpler method. They noted that its ultraviolet absorption spectrum was not identical with that given by Falconer and Gulland. No explanation was offered for this discrepancy. After noting that the absorption spectrum could be reconciled with that to be expected if the ribosyl group was in the 3- or 7-position of the purine ring, they evidently retained the belief that the ribosyl group was in the 9-position and suggested that the anomalous spectrum was possibly due to an interaction between the ribose moiety and the oxygen on position 8 of the purine ring. Leone [4] has also isolated a uric acid riboside from beef blood by a method somewhat similar to that of Falconer and Gulland; the ultraviolet absorption spectrum of his compound is apparently very similar, qualitatively at least, to that of the material isolated by Carter and Potter.

In an attempt to resolve the contradictions in the published data on uric acid riboside, we have isolated this compound from beef blood by a simple method and have reinvestigated some of its properties. The conclusion drawn from this work is that the uric acid riboside isolated by Carter and Potter, by Leone, and by us is not the 9-riboside but is, in fact, the 3-riboside. The evidence for this is based on comparison of the isolated material with 3-, 7-, and 9-methyluric acid by a number of techniques, including ultraviolet spectrophotometry.

The compound was isolated from an aqueous-acetone extract of beef red-blood cells by using a Dowex 1 anion-exchange column and crystallized from a gelatinous aqueous solution as colourless needles. From the elementary analysis, it appears that the compound contains 1·5 mol. of water of crystallization, only one of which is lost at 100° *in vacuo*: the only other published analysis of uric acid riboside [1] is a nitrogen analysis which corresponds to that for an anhydrous compound. A significant difference was also found in the optical rotation of our material, which had $[\alpha]_D^{25}$ −19·8° as compared with Falconer and Gulland's value [1] of $[\alpha]_D^{25}$ −40·8°, the conditions of measurement and solvent being approximately comparable.

When subjected to the action of a nucleosidase preparation [5] from the bacterium *Lactobacillus pentosus*, the compound was degraded to uric acid and a sugar, which was quantitatively estimated by Nelson's method [6] as used by Wang,[7] and shown to be identical with ribose by paper chromatography. As would be expected for a ribofuranoside, the compound consumed one mol. of sodium metaperiodate. All these results indicate that our compound is a uric acid riboside.

Evidence for the position of attachment of the ribosyl group was obtained by comparison of the isolated material with uric acid derivatves (3-, 7-, and 9-methyl- and 9-2′-hydroxyethyl-uric acid) in as many different ways as could be devised. All of these compounds and uric acid give colour reactions with *N*,2,6-trichlorobenzoquinone imine [8] which appear to be characteristic of the unsubstituted compound and of the position of nitrogen-substitution. The colour can be developed by spraying the reagent on paper chromatograms, and the test is made more sensitive by subsequent spraying with a slightly alkaline buffer. The colour reactions given by the various compounds are recorded in Table 1. Uric acid riboside gives a yellow colour with this reagent which is similar to that given by 3-methyluric acid and is distinguishable from those of all the other compounds.

Comparison of the ultraviolet spectrum of uric acid riboside with those of the model compounds at different pH values (Fig. 1 and Table 2) confirmed the close structural resemblance between this compound and 3-methyluric acid and revealed obvious differences from 9-methyluric acid, though the spectra of all the compounds are rather similar. From the data available,[4,9] it appears that Carter and Potter's compound and Leone's compound

[4] Leone, *Boll. Soc. ital. Biol. sper.*, 1955, **31**, 622.
[5] Lampen and Wang, *J. Biol. Chem.*, 1952, **198**, 385.
[6] Nelson, *J. Biol. Chem.*, 1944, **153**, 375.
[7] Wang in "Methods in Enzymology," Vol. II, ed. Colowick and Kaplan, Academic Press, Inc., New York, 1955, p. 456.
[8] Berry, Sutton, Cain, and Berry, *Univ. Texas Publ. No.* 5109, 1951, 22.
[9] Unpublished spectrum supplied by Dr. C. E. Carter.

have the same ultraviolet absorption spectrum as the uric acid riboside described in this paper.

Uric acid is known to decompose rapidly in alkaline solution,[10] and 3-, 7-, and 9-methyluric acid behave similarly. This provided an additional method of comparison, since the rates of decomposition could be conveniently followed by measuring the decrease in ultraviolet absorption at the maxima of the various compounds with time. Thus,

TABLE 1. *Summary of chromatographic data on uric acid derivatives* [a] *in various solvents.*

Compound	Propan-1-ol–1% aq. NH_3 (3 : 2)	NMe_2·CHO–Bu^nOH–H_2O (1 : 1 : 1)	Bu^nOH–AcOH–H_2O (4 : 1 : 1)	Bu^nOH–H·CO_2H–H_2O (8 : 2 : 5)
Uric acid [b]	0·37, Y–O, O	0·51, Y–O, O	0·17, Y–O, O	0·42, NC, O
Uric acid riboside	0·48, R–P, Y	0·63, R–P, Y	0·16, NC, Y	0·53, NC, Y
3-Methyluric acid	0·47, NC, Y	0·60, NC, Y	0·28, NC, Y	0·54, NC, Y
7-Methyluric acid	0·48, R–B, R–B	0·60, Y–B, R–B	0·32, Y–B, R–B	0·64, NC, R–B
9-Methyluric acid	0·48, Y, Y–O	0·59, Y, Y–O	0·26, NC, Y–O	0·41, NC, NC
9-2′-Hydroxyethyluric acid	0·48, Y–B, Y–O	0·57, Y, Y–O	0·21, Y, Y	0·51, NC, Y

[a] R_F values (1st column) and colour reactions with *N*,2,6-trichloroquinone imine before (2nd column) and after (3rd column) spraying with buffer. NC, no colour; Y, yellow; O, orange; R, red; B, brown; P, purple. [b] Leone and Guerritorie (*Boll. Soc. ital. Biol. sper.*, 1950, **26**, 609; *Chem. Abs.*, 1951, **45**, 7621) used different solvent systems to separate uric acid and uric acid riboside.

TABLE 2. *Ultraviolet absorption spectra.*

Compound	pH of solvent	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	$\lambda_{min.}$ (mμ)	$10^{-3}\varepsilon$
7-Methyluric acid	1	286, 234	11·1, 8·6	258, 214	3·7, 5·0
	7	294, 238	12·1, 10·2	263, 219	3·3, 6·4
	14	297	13·6	263	2·8
3-Methyluric acid	1	288, 233	11·3, 8·3	258, 215	3·2, 5·2
	7	296, 241 (sh.)	16·0, 4·4	262	2·7
	14	292, 245 (sh.)	15·3, 3·2	256	2·6
Uric acid riboside	1	288, 233	12·4, 6·8	256, 220	2·9, 5·7
	7	298, 243 (infl.)	17·7, 2·9	257	2·3
	14	297	16·5	254	1·6
9-Methyluric acid	1	286, 233	13·0, 7·9	256, 215	3·7, 4·7
	7	292, 238	11·9, 9·2	262, 224	2·7, 5·6
	14	299, 250	10·3, 9·9	272, 228	4·5, 4·4
9-2′-Hydroxyethyluric acid	1	287, 233	12·6, 7·5	256, 215	3·3, 4·2
	7	292, 238	11·7, 9·1	263, 224	2·5, 5·6
	14	301, 249	9·9, 9·7	273, 228	3·9, 4·0

TABLE 3. *Calculated* [a] pK_a *values of uric acid derivatives.*

Compound	pK_a values	
Uric acid riboside	6·0	10·9
3-Methyluric acid	6·1	11·3
9-Methyluric acid [b]	5·6	11·3
7-Methyluric acid	5·4	10·6
Uric acid [b]	5·4	11·3

[a] Cf. Fox and Wempen, *Adv. Carbohydrate Chem.*, 1959, **14**, 304. [b] Slightly different values are given by Bergmann and Dikstein (*J. Biol. Chem.*, 1922, **54**, 601).

9-methyluric acid (and 9-2′-hydroxyethyluric acid) decomposed the fastest and 7-methyluric acid the slowest. 3-Methyluric acid and uric acid riboside decomposed in alkali at intermediate, and almost identical, rates (Fig. 2).

Finally, p*K* values for the model compounds and uric acid riboside were calculated by the spectrophotometric method described by Shugar and Fox.[11] Although the evidence (Table 3) is not so clear cut in this case, it is again apparent that the values for uric acid riboside most closely resemble those for 3-methyluric acid.

[10] Griffiths, *J. Biol. Chem.*, 1952, **197**, 399; Albert and D. J. Brown, *J.*, 1954, 2060.
[11] Shugar and Fox, *Biochim. Biophys. Acta*, 1952, **9**, 199.

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By these four criteria, the uric acid riboside which we have isolated from beef blood resembles 3-methyluric acid most closely and is quite clearly different from the 7- and the 9-methyl compound. It seems therefore that it should be described as the 3-isomer. We are attempting to provide final confirmation of this by synthetic means.

FIG. 1. *Ultraviolet absorption spectra of 9-methyluric acid* (A), *uric acid riboside* (B), *3-methyluric acid* (C), *and 7-methyluric acid* (D). *The spectra are arranged without regard to their specific absorbancies to show clearly the relative positions of the maxima and minima.*

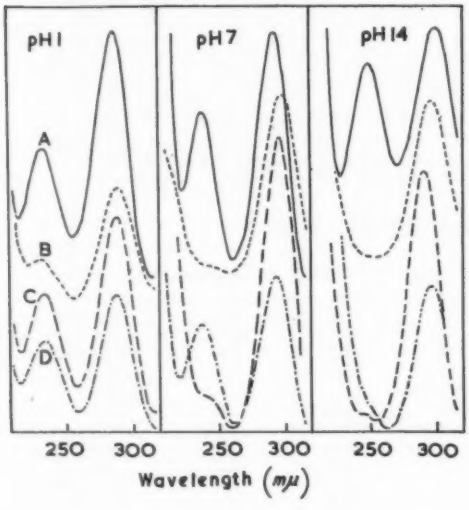
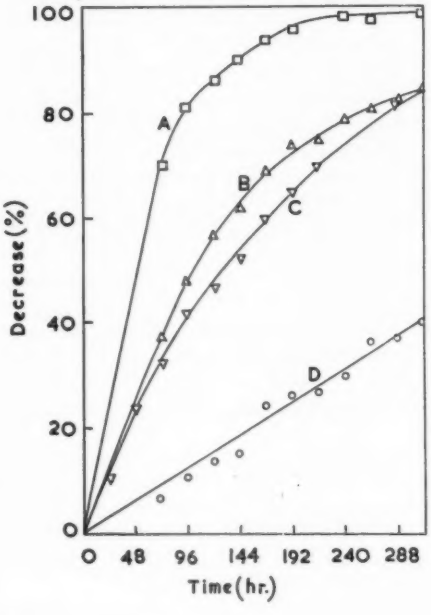


FIG. 2. *Decomposition of 9-methyluric acid* (A), *uric acid riboside* (C), *3-methyluric acid* (B), *and 7-methyluric acid* (D), *in 0·1N-sodium hydroxide expressed as percentage decrease in heights of the longer-wavelength maxima.*



EXPERIMENTAL

Isolation of Uric Acid Riboside.—Fresh, defibrinated beef blood (2 l.) was centrifuged at 6000 r.p.m. for 15—20 min. The packed red-blood cells were resuspended in physiological saline solution and again collected by centrifugation. Acetone (1·2 l.) and water (120 ml.) were then added to the packed mass, and the whole was heated gently on the steam-bath with stirring until the precipitated solids became dark brown (5—10 min.). An additional quantity of water (500 ml.) was added and most of the solid was removed by filtration through cheese-cloth. The solution was finally clarified by filtration through Celite.

This extract was concentrated to about 250 ml. and again filtered through Celite. The clear filtrate was added to a column (20 × 2 cm.) of Dowex 1 anion-exchange resin in the acetate form. The column was washed with ammonium acetate solution (0·6N-ammonia adjusted to pH 8 with acetic acid; 200 ml.), then with water (500 ml.), and finally with 0·01M-acetic acid (500 ml.). The eluate from the last two washings contained no material absorbing at 310 mμ. Elution was then commenced with 0·02M-acetic acid; after about 350 ml. of this had passed through the column, the absorption of the eluates at 310 mμ began to rise, reached a maximum, and then declined. The fractions containing the absorbing material were combined (800 ml.) and evaporated *in vacuo*. The residue was dissolved in hot water (10 ml.) and the solution set aside, whereupon it became gelatinous. Over a period of days masses of colourless needles separated; these were collected by filtration (50—60 mg.). A further quantity of material (20—30 mg.) was obtained by combining the mother-liquors and end-fractions from the column and repurifying them through a second column.

Small amounts of material (5—10 mg.) were isolated by paper chromatography of the concentrated aqueous acetone extracts on heavy filter paper (Whatman No. 17; 1 rectangular sheet/*ca.* 12 ml. of extract). After development of the chromatogram with butan-1-ol–dimethylformamide–water (1 : 1 : 1), the appropriate band was detected by its ultraviolet absorption or by the use of a *N*,2,6-trichlorobenzoquinone imine spray on a representative strip of the chromatogram, cut out, and eluted with water, and the material was rechromatographed with propan-1-ol–1% aqueous ammonia (3 : 2) as solvent. This gave an amorphous solid which was shown to be about 70% pure by its specific ultraviolet absorption.

The chromatographic technique was used to show that uric acid riboside was the sole uric acid-containing compound present in beef red-blood cells (cf. Benedict [12]); it did not occur in blood serum, which however contained small amounts of uric acid.

A portion of the crystalline material, recrystallized from water for analysis and dried at 25° *in vacuo* over phosphorus pentoxide, had m. p. >350°, $[\alpha]_D^{25}$ −19·8° (*c* 2·13 in 0·1N-NaOH) (Found: C, 36·8; H, 4·6; N, 16·7. $C_{10}H_{12}N_4O_7,1{\cdot}5H_2O$ requires C, 36·8; H, 4·6; N, 17·1. Found, after drying at 120°/2 mm.: C, 39·4; H, 3·9; N, 18·1. $C_{10}H_{12}N_4O_7,0{\cdot}5H_2O$ requires C, 39·0; H, 4·2; N, 18·1%).

Paper Chromatography.—The R_F values of the above material in a variety of solvents are listed in Table 1, with data for uric and methyluric acids.

Periodate Oxidation of Uric Acid Riboside.—Crystalline material was oxidized with sodium metaperiodate, the spectrophotometric microtechnique of Dixon and Lipkin [13] being used to determine the uptake of oxidant. One mol. of oxidant was consumed in 5 min., after which oxidation ceased.

Identification of Cleavage Products from Uric Acid Riboside.—Uric acid riboside (1·44 mg.) was incubated at 37° with a crude enzyme preparation from *L. pentosus* [*Lactobacillus planatarum* (*pentosus*), strain 124-2, ATCC 8041]. After 4 hr. the reducing sugar was quantitatively estimated in aliquot parts of the solution (which were calculated to contain initially 0·24 mg. of uric acid riboside) by the method of Nelson [6] as described by Wang.[7] The yield was 0·100 mg.; theor., 0·106 mg.

In another experiment, after incubation the protein was precipitated by heating its solution at 100° for 3 min. and the clear supernatant liquid was subjected to paper chromatography, with appropriate controls. The sole ultraviolet-absorbing material present was shown to be uric acid (appropriate solvents listed in Table 1), and the reducing sugar was identical with ribose (butan-1-ol–acetic acid–water; 4 : 1 : 1).

The compound was readily hydrolyzed by N-hydrochloric acid (66% after 1 hr. at 100° as measured by the production of uric acid). Falconer and Gulland's results [1] seem to indicate that their compound was much more stable to hydrolysis (6 hr. in 16% sulphuric acid for complete hydrolysis).

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of uric acid riboside and the model compounds are shown in Fig. 1. These are arranged arbitrarily to make the similarities and differences among the maxima and minima more easily discernible. The extinction coefficients for these compounds and 9-2′-hydroxyethyluric acid are given in Table 2.

Alkaline Decomposition of Uric Acid Derivatives.—The rates of decomposition of uric acid riboside and 3-, 7-, and 9-methyluric acid in 0·1N-sodium hydroxide at 25°, as measured by the percentage decrease in heights of the longer wavelength maxima, are recorded in Fig. 2. 9-2′-Hydroxyethyluric acid decomposed at the same rate as 9-methyluric acid. No attempt was made to elucidate the mechanism of decomposition of these compounds.

p*K Values.*—The p*K* values of the compounds were determined by the spectrophotometric method,[11] and the results are given in Table 3.

To provide a second example of a 9-substituted derivative, 9-2′-hydroxyethyluric acid was synthesized in an unambiguous manner from 2,4-dihydroxy-6-2′-hydroxyethylaminopyrimidine. In the comparisons described above, it behaved exactly as the 9-methyl compound; therefore, to avoid confusion it was not included in the Figures.

9-2′-Hydroxyethyluric Acid.—5-Amino-2,4-dihydroxy-6-2′-hydroxyethylaminopyrimidine bisulphite compound was prepared from 2,4-dihydroxy-6-2′-hydroxyethylaminopyrimidine (500 mg.) according to Masuda's procedure.[14] Without isolation of the product, the mixture

[13] Benedict, *J. Biol. Chem.*, 1915, **20**, 633.
[13] Dixon and Lipkin, *Analyt. Chem.*, 1954, **26**, 1092.
[14] Masuda, *Pharm. Bull.* (*Japan*), 1957, **5**, 28; McNutt, *J. Amer. Chem. Soc.*, 1960, **82**, 217.

was concentrated *in vacuo* at 25°, 10% aqueous sodium hydroxide (9 ml.) was added, and carbonyl chloride was bubbled through the solution, which was kept in an ice bath, for 0·75 hr.[15] The precipitate, which began to separate immediately on addition of the carbonyl chloride, was isolated by filtration and washed with cold water. The filter cake was dissolved in a minimum of warm 0·1N-sodium hydroxide; on acidification of the warm solution with glacial acetic acid, clusters of white needles separated [146 mg., overall yield 23·6%; m. p. >350° (decomp.)] (Found: N, 26·3. $C_7H_8N_4O_4$ requires N, 26·4%).

Discussion

There is no doubt that we have isolated the major uric acid-containing compound in beef red-blood cells. Two other investigators also appear to have isolated this compound. The question still remains—how did Falconer and Gulland obtain a compound from beef blood (and beef liver) whose ultraviolet absorption spectrum closely resembled that of 9-methyluric acid? We have repeated Falconer and Gulland's experimental procedure as closely as possible, reasoning that possibly some step in this method was causing a rearrangement of the uric acid riboside. We could find no evidence of the appearance of a riboside different from the one we have isolated. There is the possibility that under unusual dietary conditions (*e.g.*, a high-protein diet) uric acid-9 riboside could occur in beef blood, and the most reasonable conclusion, then, would be that Falconer and Gulland, by chance, obtained their blood from cattle under such dietary conditions. An alternative possibility that a different uric acid riboside occurs in different breeds of cattle seems to be scarcely feasible. A fortuitous contamination of uric acid with ribose cannot be ruled out, although the ultraviolet absorption spectral evidence would appear to eliminate this possibility. Further, and contrary to a previous report,[16] we could find no paper-chromatographic evidence that a uric acid riboside occurs in human, chicken, or pig blood.

In beef blood, uric acid riboside occurs only in the red blood cells. Presumably it is used metabolically as a more soluble " carrier " for uric acid from the tissues to the kidney. There is no evidence that it is concerned with or derived from the other purine nucleosides in the biochemical processes in which they are involved. Therefore, it is not unreasonable that its structure should differ from those of the other naturally occurring purine nucleosides and it might even be predicted that in mammalian blood containing this riboside, specific enzymes would be involved in its synthesis and/or degradation. An enzyme preparation obtained from various human tissues and from a number of other mammalian tissues [17,18] is capable of splitting uric acid riboside, but its specificity has not been determined. Obviously this problem warrants further study, especially in view of the structural evidence for uric acid riboside presented in this paper.

We are grateful to Dr. W. Pfleiderer and Professor H. Bredereck for gifts of 3-, 7-, and 9-methyluric acid, to Dr. W. S. McNutt for a gift of the intermediate used in the synthesis of 9-2′-hydroxyethyluric acid, and to Dr. C. E. Carter for a sample of uric acid riboside isolated by him and for a record of its absorption spectrum. This work was supported by a PHS research grant, RG-6492, from the National Institutes of Health, Public Health Service, and by the Robert A. Welch Foundation, Houston, Texas.

Genetics Foundation, The University of Texas,
Austin 12, Texas, U.S.A. [*Received, October 3rd*, 1960.]

[15] Cavalieri and Bendich, *J. Amer. Chem. Soc.*, 1950, **72**, 2587.
[16] Newton and Davis, *J. Biol. Chem.*, 1922, **54**, 601.
[17] Laster and Blair, *Fed. Proc.*, 1958, **17**, 261.
[18] Laster and Blair, *J. Clin. Invest.*, 1958, **37**, 909.

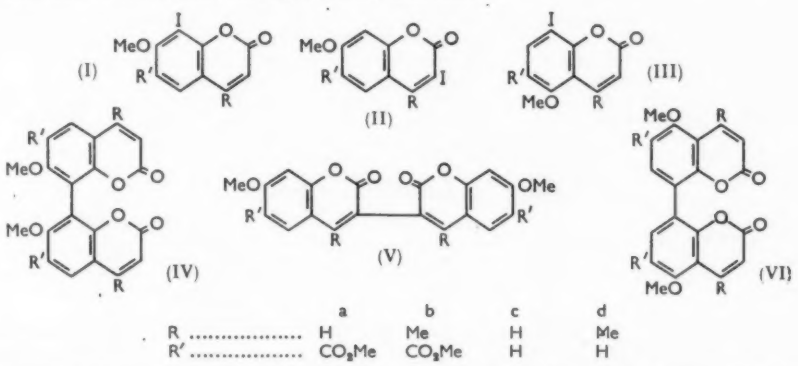
200. *Synthesis of Some Bicoumarinyl and 8-Phenylcoumarin Derivatives.*

By S. S. Lele, M. G. Patel, and Suresh Sethna.

Several 3,3′- and 8,8′-bicoumarinyls have been synthesised by the Ullmann reaction on iodocoumarins; and 8-phenylcoumarins have been synthesised by the crossed Ullmann reaction between iodocoumarins and iodobenzene.

Dey and Row [1] prepared 4,3′-bicoumarinyls by condensation of various phenolic aldehydes with 4-coumarinylacetic acids. Huebner and Link [2] reported the formation of the bicoumarinyl derivative from 3-bromo-4-methoxycoumarin by the Ullmann reaction. No other work on the synthesis of bicoumarinyls appears to have been reported. Further, 8-phenylcoumarins have not hitherto been prepared. The present paper reports the synthesis of several bicoumarinyl and 8-phenylcoumarin derivatives from the monoiodocoumarins by the Ullmann reaction.

Methyl 8-iodocoumarin-6-carboxylates (Ia and b), (IIa and b) and (IIIb), when treated with copper bronze in boiling diphenyl ether, yielded the corresponding bicoumarinyl esters (IV—VI), and these on hydrolysis and decarboxylation gave the compounds (IVc and d), (Vc and d), and (VId), respectively, identical with those obtained from the Ullmann reaction on iodocoumarins (Ic and d), (IIc and d), and (IIId). These bicoumarinyls were demethylated to the corresponding hydroxy-derivatives.



	a	b	c	d
R	H	Me	H	Me
R′	CO_2Me	CO_2Me	H	H

Attempts to prepare the (—)-brucine salt of the acids from the bicoumarinyl esters (IVa and b), to see if they could be resolved into optical isomers, did not succeed on account of the sparing solubility of the acids in various solvents.

Crossed Ullmann reaction between iodobenzene and the iodocoumarin esters (Ia and b) yielded mixtures from which the corresponding 8-phenylcoumarin derivatives were isolated by fractional crystallisation. The esters were hydrolysed and decarboxylated to the simple 8-phenylcoumarin derivatives, which were also obtained by Ullmann reaction between iodobenzene and the iodocoumarins (Ic and d) respectively.

5-Methoxy-4-methyl-8-phenylcoumarin was similarly obtained from the iodocoumarin (IIId).

Experimental

Synthesis of Bicoumarinyls (*Table* 1).—The iodocoumarin [3] (0·01 mole) was refluxed in diphenyl ether with copper bronze (0·03 mole) for 2 hr. The mixture was then filtered. The

[1] Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 107.
[2] Huebner and Link, *J. Amer. Chem. Soc.*, 1945, **67**, 99.
[3] Lele and Sethna, *J. Org. Chem.*, 1958, **23**, 1731; Lele, Patel, and Sethna, *J. Indian Chem. Soc.*, in the press.

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product which separated on dilution of the filtrate with light petroleum was dissolved in hot glacial acetic acid and allowed to cool. The sparingly soluble bicoumarinyl derivative separated and was further crystallised from the same solvent. The mother-liquor yielded the original but de-iodinated coumarin. The *bicoumarinyl derivatives* were very sparingly soluble in common solvents such as alcohols, acetone, acetic acid, benzene, and ether.

Synthesis of 8-Phenylcoumarins (*Table* 2).—A mixture of iodocoumarin (0·01 mole), iodobenzene (0·02 mole), and copper bronze (0·04 mole) was heated at the temperature mentioned in Table 2 for 3 hr., then extracted with light petroleum (to remove biphenyl) and then several

TABLE 1. *Bicoumarinyl derivatives.*

Bicoumarinyl	M. p.	Yield (%)	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
IVc	376°	48	68·1	4·4	$C_{20}H_{14}O_6$	68·6	4·1
Vc	295	25	68·3	4·2	$C_{20}H_{14}O_6$	68·6	4·1
IVa	268	63	61·7	4·2	$C_{24}H_{18}O_{10}$	61·8	3·9
Va	326	16	61·3	4·3	$C_{24}H_{18}O_{10}$	61·8	3·9
IVd	358	68	69·5	4·9	$C_{22}H_{18}O_6$	69·8	4·8
Vd	268	17	69·8	4·8	$C_{22}H_{18}O_6$	69·8	4·8
IVb	250	64	63·0	4·5	$C_{26}H_{22}O_{10}$	63·2	4·4
Vb	286	20	63·2	4·2	$C_{26}H_{22}O_{10}$	63·2	4·4
VId	>400	8	69·4	5·2	$C_{22}H_{18}O_6$	69·8	4·8
VIb	353	12	63·2	4·6	$C_{26}H_{22}O_{10}$	63·2	4·4

TABLE 2. *8-Phenylcoumarin derivatives.*

Reaction temp.	8-Phenylcoumarin	M. p.	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
220—225°	7-OMe	128—130°	75·6	4·9	$C_{16}H_{12}O_3$	76·2	4·8
*	7-OMe-6-CO_2Me	120—121	69·9	4·7	$C_{18}H_{14}O_5$	69·7	4·5
220—225	7-OMe-4-Me	158	76·3	4·9	$C_{17}H_{14}O_3$	76·7	5·3
*	7-OMe 4-Me-6-CO_2Me	168	70·5	5·0	$C_{19}H_{16}O_5$	70·4	4·9
260—265	5-OMe-4-Me	156—158	76·8	5·1	$C_{17}H_{14}O_3$	76·7	5·3

* In boiling nitrobenzene for 3 hr.

TABLE 3. *Demethylation products.*

Cpd.* but with OH replacing OMe	M. p.	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
IVc	390°	66·9	3·2	$C_{18}H_{10}O_6$	67·1	3·1
Vc	>400	67·3	3·5	$C_{18}H_{10}O_6$	67·1	3·1
IVd	366	68·7	4·3	$C_{20}H_{14}O_6$	68·6	4·0
Vd	>400	68·7	4·4	$C_{20}H_{14}O_6$	68·6	4·0
VId	>400	68·5	4·2	$C_{20}H_{14}O_6$	68·6	4·0
†	184	76·6	4·9	$C_{16}H_{12}O_3$	76·2	4·8

* In alkaline solution, the first four compounds show no fluorescence, the fifth gives a deep yellow colour, and the sixth shows intense blue fluorescence. † 7-Hydroxy-4-methyl-8-phenylcoumarin.

TABLE 4. *Hydrolysis products.*

Cpd.* but with CO_2H replacing CO_2Me	M. p.*	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
IVa	310°	60·8	3·6	$C_{22}H_{14}O_{10}$	60·3	3·2
Va	365	60·1	3·5	$C_{22}H_{14}O_{10}$	60·3	3·2
IVb	306	61·6	4·3	$C_{24}H_{18}O_{10}$	61·8	3·9
Vb	338	61·7	4·2	$C_{24}H_{18}O_{10}$	61·8	3·9
VIb	>400	61·6	3·7	$C_{24}H_{18}O_{10}$	61·8	3·9
†	237—238	68·5	4·3	$C_{17}H_{12}O_5$	68·9	4·1
‡	258	69·6	4·9	$C_{18}H_{14}O_5$	69·7	4·5

* All the acids dissolve in sodium hydrogen carbonate solution with effervescence and melt with effervescence. † 7-Methoxy-8-phenylcoumarin-6-carboxylic acid. ‡ 7-Methoxy-4-methyl-8-phenylcoumarin-6-carboxylic acid.

times with boiling acetone. The products obtained on removal of acetone from the extracts and fractional crystallisation were the *8-phenylcoumarin derivatives*. For the esters (Ia and b) nitrobenzene was used as solvent, and the 8-phenylcoumarin derivatives were isolated by

fractional crystallisations of the residue remaining on removal of nitrobenzene by steam-distillation.

Demethylations.—Demethylations were carried out by refluxing the compounds in acetic anhydride with hydriodic acid (*d* 1·7) at 120—130° for 2 hr. The *products* are listed in Table 3.

Hydrolyses.—The esters were hydrolysed by refluxing 10% alcoholic potassium hydroxide in 2 hr. The *acids* are listed in Table 4.

Decarboxylations.—The bicoumarinyl acids were decarboxylated by refluxing them in quinoline with copper powder for 0·5 hr. The 8-phenylcoumarincarboxylic acids were heated in quinoline with copper powder at 200°.

One of us (M. G. P.) thanks the Government of India for a research scholarship.

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201. *Hydrothermal Chemistry of the Silicates. Part IX.* Nitrogenous Aluminosilicates.*

By R. M. BARRER and P. J. DENNY.

By hydrothermal reaction, a number of crystalline ammonium and alkylammonium aluminosilicates have been synthesised. These are often of types analogous to alkali metal aluminosilicates and include ammonium analcites, harmotomes and micas. From methylammonium aluminosilicate gels, nitrogenous micas, montmorillonoid clays, harmotomes, sodalites, faujasites and Linde molecular sieve A were prepared. Under hydrothermal conditions methylammonium ions hydrolysed in part; but in appropriate methanol–water mixtures methylation of the ammonium base occurred. Hydrolysis and methylation of the organic base were found to play a part in determining the nitrogenous aluminosilicates produced. The ease of crystallisation tended, in the reaction mixtures used, to be correlated with the dissociation constants of the organic bases present. The crystals produced have been characterised in various ways.

Other phases identified included cristobalite, corundum, boehmite, and bayerite. Some mullite appeared when ammonium mica and certain of the methylammonium montmorillonites were sintered.

SEVERAL studies [1-4] from these laboratories have been particularly concerned with the crystallisation fields under hydrothermal conditions of lithium, sodium, potassium, rubidium, cæsium and thallium aluminosilicates, and with the properties and structures of the crystals produced. A limited study has also been made of the formation of germanium and gallium analogues of sodium aluminosilicates.[5] In the present paper we report conditions for synthesis of nitrogenous crystalline aluminosilicates in which there are no metal cations, but only ammonium or methylammonium ions. The literature contains little reference to such a possibility, although Merrill and Spencer [6] reported the formation of quaternary ammonium silicates such as $(NMe_4)HSiO_3,5H_2O$.

EXPERIMENTAL

Methylammonium hydroxides were employed as appropriately concentrated aqueous solutions. Mono-, di-, tri-, or tetra-methylammonium, or ammonium, hydroxide was stirred

* Part VIII, *J.*, 1959, 195.

[1] Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.
[2] *E.g.*, Barrer and Langley, *J.*, 1958, 3804, 3811, 3817.
[3] Barrer, Bultitude, and Kerr, *J.*, 1959, 1521.
[4] Barrer and Kerr, *Trans. Faraday Soc.*, 1959, **55**, 1915.
[5] Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.
[6] Merrill and Spencer, *J. Phys. Colloid Chem.*, 1951, **55**, 187.

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in the correct proportions with freshly prepared amorphous alumina gel into " Syton " silica sols. In this way hydrous ammonium or alkylammonium aluminosilicate gels were produced of compositions $3(NMe_xH_{4-x}OH),Al_2O_3,nSiO_2$ + aq., where $1 < n < 9$ and $x = 0$—4. A number of these gels were relatively stiff, and often after hydrothermal treatment, especially at lower temperatures, the filtrates contained colloidal material amorphous to *X*-rays. The base was provided in excess of the 1 : 1 ratio between it and alumina to maintain the pH and so to promote dissolution and recrystallisation of solids.

The aqueous gels were heated in stainless steel autoclaves of about 16 c.c. capacity. After reaction the autoclaves were chilled rapidly, and the solids filtered off, washed, and dried. The solids were then examined optically, in the electron microscope, by electron diffraction, and by *X*-ray diffraction, as necessary. By these means they were normally identified according to the structures of the aluminosilicate frameworks. In some instances the crystals were further characterised by thermogravimetry and by differential thermal analysis. Some details of the equipment and procedures used in this examination have been briefly described in earlier papers.[2]

Results

Crystallisation of Ammonium Aluminosilicates.—The species identified are given in Table 1. There were three nitrogenous aluminosilicates, based on the three-dimensional network zeolites analcite and harmotome, and on the layer-lattice of mica, severally. These minerals were formed in highly alkaline conditions, since the pH's of the cold mother-liquors after reaction were > 10·5 in all cases. The crystallisation of ammonium harmotome was poor, so that its *X*-ray pattern was not suitable for its full identification; however, the few lines obtained showed correspondence with this zeolite. Although the material termed NH_4-H (see Table 1) is similar to cristobalite, some weak *X*-ray diffractions were also present which indicated a further, unidentified species. *d*-Spacings of this species and of NH_4-H are given in Table 2. The crystallisation conditions are summarised in Table 3 and emphasise the dominance of the micaceous crystals throughout the crystallisation field.

TABLE 1. *Crystalline phases in the ammonium aluminosilicate field.*

Symbol	Identification	Yields	Symbol	Identification	Yields
NH_4-A	Boehmite	Fair	NH_4-H	Cristobalite	Fair
NH_4-B	Corundum	Poor	NH_4-K	Mica	V. good
NH_4-D	Cubic NH_4-analcite	Fair to poor	NH_4-L	Harmotome	V. poor

TABLE 2. d-*Spacings* (*in* Å) *of some ammonium aluminosilicates.*

NH_4-D (analcite)				NH_4-H (cristobalite)		Unidentified phase occurring with NH_4-H	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
5·54	s	$2·40_7$	vw	$4·02_5$	vs	4·24	w
4·81	mw	$2·20_1$	w	$3·12_6$	m	$3·73_8$	vw
3·63	vw	$1·88_3$	w	$2·83_7$	ms	$3·51_8$	vw
$3·39_3$	vs	$1·72_3$	m	$2·11_1$	mw	$3·23_7$	vw
$3·02_8$	vw	$1·60_6$	m	$2·01_3$	w	$3·19_1$	vw
$2·89_5$	ms	$1·57_9$	w	$1·92_7$	mw	$1·34_4$	w
$2·66_5$	vw	$1·43_0$	w	$1·86_6$	mw	$1·33_1$	vw
$2·49_6$	mw			$1·53_1$	w		

NH_4-D. This species was a cubic variety of analcite having a unit cell edge 13·57 Å. It appeared at 450° c at times between 7 and 11 days. The *d*-spacings are recorded in Table 2.

NH_4-K. The micaceous species, NH_4-K, resembles the illites about as closely as the muscovites. The *d*-spacings are compared with those of illite and of muscovite in Table 4. The monoclinic unit cell dimensions were: $a = 5·22$; $b = 9·02$; $c = 20·02$ Å; $\beta = 95°\ 27'$. It was obtained in 100% yield, the best conditions being at 450° for $n = 2$. Differential thermal analysis curves are shown in Fig. 1*a* and b_1, and the corresponding thermogravimetric curve in Fig. 2*a*. Up to about 300° the weight loss is 1·3%, being endothermic. The material lost

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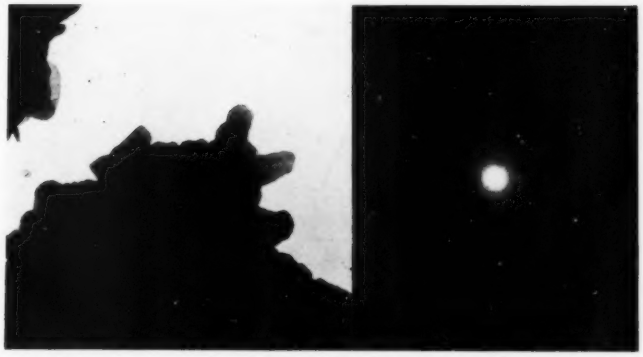
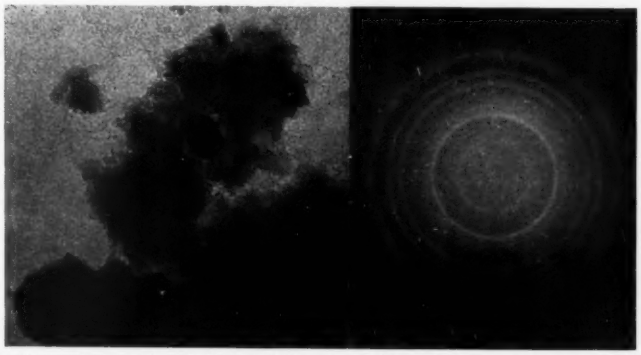
PLATE I.

(*a*) (*b*)



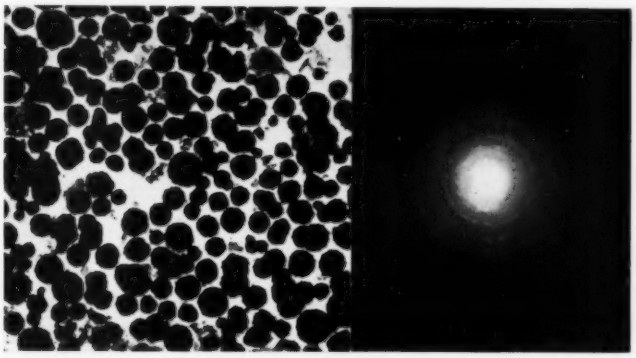
a and b, Photomicrograph and electron diffraction pattern of ammonium mica.

(*c*) (*d*)



c and d, Photomicrograph and electron-diffraction pattern of nitrogenous montmorillonite.

(*e*) (*f*)



e and f, Photomicrograph and electron-diffraction pattern of nitrogenous hermotome.

[*To face p.* 972.

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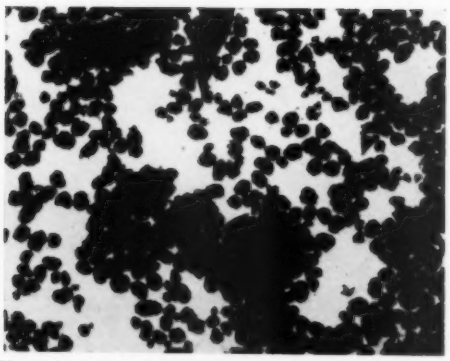
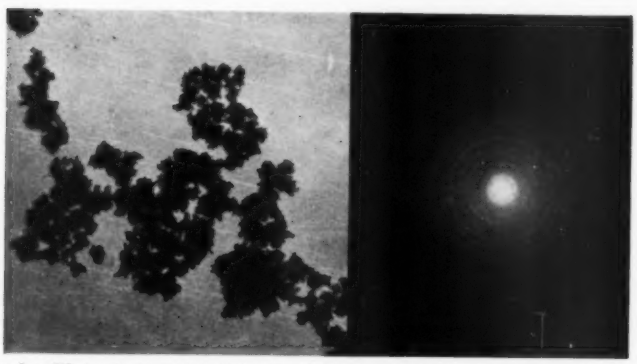
PLATE 2.

(*a*)



a, Photomicrograph of nitrogenous Linde molecular sieve A.

(*b*)



(*c*)

b and c, Photomicrograph and electron-diffraction pattern of nitrogenous faujasite.

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TABLE 3. *Crystallisation conditions for gels* $3NH_4OH,Al_2O_3,nSiO_2$ + aq., *and yields.*

n	200° 6 days	250° 4 days	271° 6 days	300° 3 days	350° 2 days	400° 2 days	450° 2 days	450° 7 days	450° 11 days
1	U *	Poor A Poor K	Fair A Fair K	Fair A Fair K	Fair A Fair K	Fair A Fair K	Good K Poor B	—	—
2	U	Poor K	Good K	Good K	V. good K	V. good K	V. good K	Good K	Good K
3	U	U	Fair K	Fair K	Good K	Good K	Good K	—	—
4	U	U	V. poor K	Fair K	Good K	Good K	Good K	Good K	Good K Fair H Poor D
5	U	U	V. poor L	V. poor K	Poor K	Fair K	Fair K	—	—
6	U	U	V. poor L	V. poor L	V. poor K	Poor K	Fair K	—	Fair K Fair H Fair D
7	U	U	U	U	U	V. poor K	Fair K	—	—
8	U	U	U	U	U	V. poor K	Poor K	—	—
9	U	U	U	U	U	U	V. poor K	—	—

* U denotes non-crystalline. The terms " poor," " fair," and " good " in this and similar Tables refer to the yields of the crystals. Yields were estimated visually, and from the intensities of the *X*-ray diffraction patterns. For A, B, D, H, K, L see Table 1.

below 300° is considered to be water. The main weight loss is associated with a strong endothermic peak, while at ~980° a sharp exothermal reaction occurs which yields mullite. The total weight loss at temperatures approaching 1000° corresponds with the formula

$$\tfrac{1}{2}(NH_4)_2O,Al_2O_3,2SiO_2,\tfrac{2}{3}H_2O(\text{structural}),0{\cdot}17H_2O(\text{surface})$$

A microanalysis showed that a specimen of NH_4-K, crystallised at 300°, contained 5·15% of nitrogen, compared with a theoretical value of 6·04% for the above formula.

TABLE 4. d-*Spacings of species* NH_4-K, *and of muscovite and illite.*

hkl	*d*-Spacing (Å) and intensity: Muscovite [7]		NH_4-K		Illite [7]		*hkl*	*d*-Spacing (Å) and intensity: Muscovite [7]		NH_4-K		Illite [7]	
002	9·99	s	10·37	s	9·98	s	$13\bar{3}$	$2{\cdot}37_9$	m	—	—	2·38	m
004	4·98	m	5·17	m	4·97	w	221	$2{\cdot}24_5$	w	$2{\cdot}25_6$	vw	2·24	m
110	4·47	vs	4·50	vs	4·47	s	$22\bar{3}$	$2{\cdot}18_5$	w	$2{\cdot}18_0$	vw	2·18	w
111	4·29	w	4·36	m	—	—	$20\bar{6}$	2·14	m(D)	—	—	—	—
022	4·11	w	—	—	4·11	vw	043	2·13	m(D)	—	—	2·11	w
112	3·95	vw	—	—	—	—	223	2·05	vw	—	—	—	—
$11\bar{3}$	3·87	m(B)	—	—	—	—	0010	$1{\cdot}99_1$	s	$1{\cdot}98_6$	vw	1·98	m
023	3·72	m	3·70	ms	3·7	vw	206	1·95	w	—	—	—	—
113	3·55	vw	—	—	—	—	$04\bar{6}$	1·83	vw	$1{\cdot}85_5$	vw	—	—
$11\bar{4}$	3·48	m	3·45	m(B)	3·4	vw	138	1·76	w	—	—	—	—
006	3·32	vs	—	—	3·31	m	$13\bar{10}$	$1{\cdot}65_4$	w	$1{\cdot}69_7$	w	1·65	w
114	3·20	ms	—	—	3·2	vw	312	1·64	m	—	—	1·64	m
$11\bar{5}$	3·1	vw	3·12	m	—	—	313	1·60	w	—	—	—	—
025	2·98	s	—	—	2·98	w	314	1·55	w	—	—	—	—
115	2·86	m	—	—	2·84	vw	1310	1·52	w	—	—	—	—
$11\bar{6}$	2·78	m	2·74	vw	—	—	060	$1{\cdot}50_4$	s	$1{\cdot}50_3$	ms	1·50	s
200	$2{\cdot}58_5$	w	—	—	—	—	335	$1{\cdot}34_4$	m	$1{\cdot}37_2$	vw	1·34	vw
$20\bar{2}$	$2{\cdot}56_0$	vs	2·56	s(B)	2·56	s	—	$1{\cdot}33_5$	w	—	—	—	—
008	2·49	w	$2{\cdot}49_5$	vw	—	—	400	1·295	w(B)	$1{\cdot}29_8$	vw	1·29	m
133	2·46	w	$2{\cdot}45_6$	w	2·44	w	0016	1·245	w(B)	$1{\cdot}24_9$	vw	1·24	w
$20\bar{4}$	$2{\cdot}39_0$	m	$2{\cdot}41_2$	w	—	—							

When material NH_4-K was crystallised at 250° from a gel containing originally only NH_3Me^+ ions (Tables 5 and 6) the thermogram, shown in Fig. 1*b*, is very similar to that of NH_4-K in Fig. 1*a*. There is no exothermal peak such as characterises the pyrolysis of organic ions (Figs. 1*c* and *d*), so that at 250° hydrolysis of monomethylammonium ions must be extensive.

From crystallisations of NH_4-K at 300°, electron diffraction gave only ring patterns, but single-crystal patterns could be obtained from a product grown at 400°. Plates 1*a* and *b* show a typical electron-micrograph and electron-diffraction photograph of the micaceous

[7] Cf. Grim, Bradley, and Brown, " X-ray Identification and Structure of Clay Minerals," Min. Soc., G.B., 1951, Chap. V.

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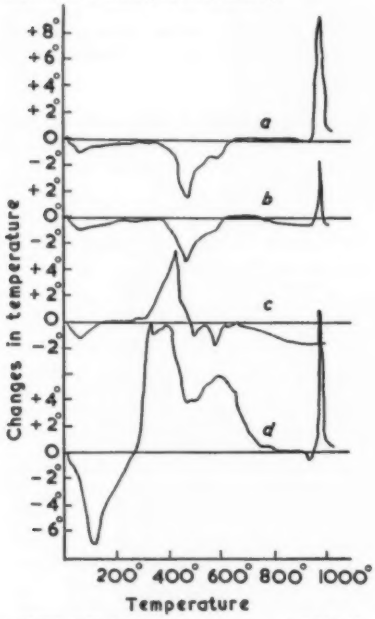
crystals. The *X*-ray powder diffraction photograph suggested that NH_4-K is dioctahedral. Thus the 060 line is close to 1·50 Å, and the 002 line is strong.

Crystallisations involving Methylammonium Bases.—The bases introduced into the gels were $NMeH_3$·OH, NMe_2H_2·OH, NMe_3H·OH, and NMe_4·OH. It became apparent that under hydrothermal conditions the substituted bases tend to be hydrolysed:

$$Me_xNH^+_{4-x} + H_2O \rightleftharpoons Me_{x-1}NH^+_{5-x} + MeOH \quad . \quad . \quad . \quad . \quad . \quad (1)$$

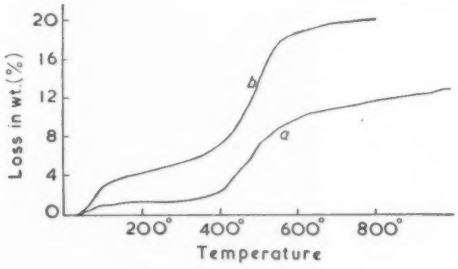
The higher the temperature the more rapidly such a hydrolysis can occur, and a series of alkylammonium ions and also NH_4^+ may result in solution. Accordingly the dominant cation in

FIG. 1. *Thermograms of ammonium micas (curves a and b) and of methylammonium montmorillonites (curves c and d).*



a: $3NH_4$·OH,Al_2O_3,$2SiO_2$ + aq. *at* 300° *for* 3 *days.*
b: $3NMeH_3$·OH,Al_2O_3,$2SiO_2$ + aq. *at* 250° *for* 4 *days.*
c: $3NH_4$·OH,Al_2O_3,$2SiO_2$ + aq. + 13% *of* MeOH *at* 300° *for* 4 *days.*
d: $3NMe_4$·OH,Al_2O_3,$2SiO_2$ + aq. *at* 300° *for* 5 *days.*

FIG. 2. *Thermogravimetric curves of ammonium mica (curve a) and of dimethylammonium harmotome (curve b).*



the crystalline products is in doubt and is represented by the symbol N in the following account. Nevertheless the products obtained depended upon the base used.

The dominant species were montmorillonoid clays and mica-like crystals. A notable feature of this behaviour was the relatively low temperature of formation of these layer-lattice compounds. In addition to the layer-lattice crystals, however, it was possible to grow three-dimensional network zeolites and a felspathoid. The species obtained are summarised in Table 5. The pH's of the cold mother-liquors after reaction were all >10·5. Crystallisations proceeded fairly easily, excellent yields of some species being obtained. In all systems the ease of crystallisation decreased as the proportion of silica to base and alumina became large. The phase N-L is analogous to the Na-Pl of ref. 5, which was a cubic harmotome. This zeolite

could be prepared by appropriate crystallisation of aluminosilicate gels containing initially all of the four methylammonium bases. Species N-Q and N-R are analogues of Na-Q and Na-R of ref. 5, and thus are nitrogenous varieties of Linde sieve A and Linde sieve X respectively.

The crystallisation fields of the various species in Table 5 are indicated in Figs. 3—6. The

TABLE 5. *Crystalline phases formed from alkylammonium aluminosilicate gels.*

Base in cold parent gel	Products Symbol	Identity	Maximum yield	Base in cold parent gel	Products Symbol	Identity	Maximum yield
$NMeH_3$·OH	N-C	Bayerite	Poor	NMe_4·OH	N-A	Boehmite	Poor
	N-K	Mica	Good (100%)		N-C	Bayerite	Fair
	N-L	Harmotome	Fair		N-T	Sodalite	Poor
NMe_2H_2·OH	N-A	Boehmite	Poor		N-V	Montmoril-lonite	Good (100%)
	N-C	Bayerite	Poor		N-L	Harmotome	Fair
	N-K	Mica	Good (100%)		N-Q	Zeolite, like Linde sieve A	Small yield, but obtained pure
	N-L	Harmotome	Good (100%)		N-R	Zeolite, analogue of faujasite	Small yield, but obtained pure
NMe_3H·OH	N-A	Boehmite	Poor				
	N-T	Sodalite	Fair				
	N-V	Montmoril-lonite	Fair to Good				
	N-L	Harmotome	Fair				

TABLE 6. *Crystallisation conditions of, and yields from, aqueous methylammonium aluminosilicate gels.*

(*a*) *Gels* $3NMeH_3$·OH,Al_2O_3,$nSiO_2$.

n	125°, 5 days 175°, 6 days 200°, 6 days	225°, 5 days	250°, 4 days	300°, 4 days
1	Poor C	Fair K Poor L	Fair K	Good K
2	U	Fair K Fair L	Good K V. poor L	Good K
3	U	U	Poor K	Poor K Good L
4	U	U	Poor K	Poor K Good L
5	U	U	V. poor K	V. poor K Poor L
6 to 9	U	U	U	U

(*b*) *Gels* $3NMe_2H_2$·OH,Al_2O_3,$nSiO_2$.

n	150°, 9 days	175°, 8 days	200°, 6 days	250°, 4 days	300°, 3 days
1	U	Fair L Poor C	Good L Poor A	Good K	Good K Poor A
2	U	Fair L V. poor C	Good L	Good K V. poor L	Good K Poor L
3	U	Poor L	Good L	Poor K Fair L	Fair K Fair L
4	U	Fair L	Good L	Poor K Fair L	Good L Poor K
5	U	Fair L	Good L	—	Good L Poor K
6	U	Poor L	Good L	U	Good L Poor K
7	U	V. poor L	Fair L	U	Good L V. poor K
8	U	V. poor L	V. poor L	U	Good L V. poor K

variety of the phases grown from gels containing tetramethylammonium hydroxide makes it expedient for reasons of clarity to give Fig. 6 in two parts. The conditions of growth and associated crystal yields are summarised in Tables 6 and 7. Of the layer lattice species it is seen that from ammonium, monomethylammonium, and dimethylammonium gels a mica-like phase is produced, whereas trimethyl- and tetramethyl-ammonium gels give montmorillonite-type clays.

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The Tetramethylammonium Aluminosilicate System.—The gels in this system were particularly prone to thixotropy. On hydrothermal treatment up to 150° the gels tended to remain stable and translucent as at room temperature. However, these gels became milky after several days (the time increasing with the silica content), owing to the formation of fine, white crystals.

FIG. 3. *Crystallisation fields of nitrogenous aluminosilicate gels derived from monomethylammonium aluminosilicate gels. Boundaries in this and subsequent figures are approximate only; the abscissae, n, equal the molar ratios* SiO_2 *to* Al_2O_3 *in the crystallising gels (also in* Figs. 4—6).

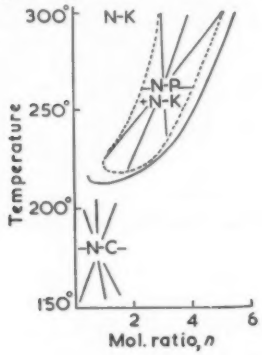


FIG. 4. *Crystallisation fields of nitrogenous aluminosilicates derived from dimethylammonium aluminosilicate gels.*

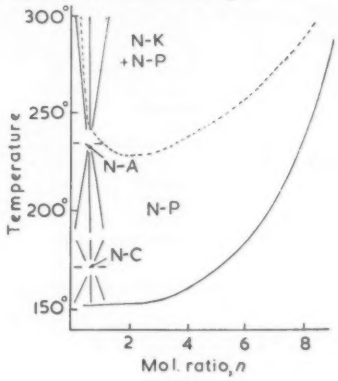


FIG. 5. *Crystallisation fields of nitrogenous aluminosilicates derived from trimethylammonium aluminosilicate gels.*

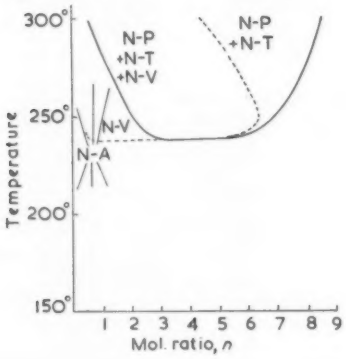
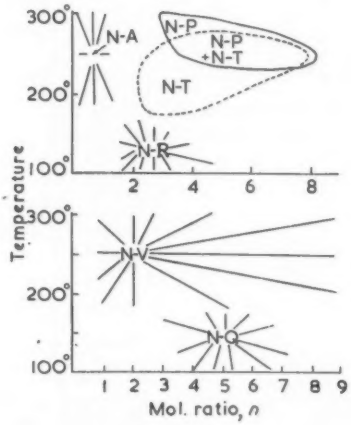


FIG. 6. *Crystallisation fields of nitrogenous aluminosilicates derived from tetramethylammonium aluminosilicate gels.*



These could be centrifuged off and although obtained only in low yield could be obtained pure. These products were the zeolites N-R and N-Q of Table 7. Gels of different concentrations were tried from about 0·75 g. dry weight to 2·0 g. dry weight per 10 ml. of water. The more concentrated gels gave larger amounts of crystals, but they also tended to solidify to stiffer gels and since no crystal separation was possible after such solidification the yield of crystalline material was limited. The gels of higher silica content ($n = 6$—9) first formed stiff gels, after about 6 days, and the other gels after progressively increasing times as n decreased.

TABLE 7. *Crystallisation conditions of, and yields from, aqueous methylammonium aluminosilicate gels.*

(*a*) *Gels* $3NHMe_3{\cdot}OH,Al_2O_3,nSiO_2$.

n	175°, 6 days	220°, 5 days	225°, 4 days	250°, 4 days	300°, 3 days
1	U	U	Poor A	Poor A Fair V	Fair L Poor T Poor V
2	U	U	U	Fair V Fair T Poor L	Fair V Poor T Poor L
3	U	U	U	Fair V Fair T Poor L	Fair T Poor L Poor V
4	U	U	U	Fair V Poor T Poor L	Fair L Fair T V. poor V
5	U	U	U	Fair V Poor T Poor L	Good L
6	U	U	U	Fair V Poor T Poor L	Good L Poor T
7	U	U	U	Poor V	Good L. V. poor T
8	U	U	U	U	Poor L V. poor T
9	U	U	U	U	U

(*b*) *Gels* $3NMe_4{\cdot}OH,Al_2O_3,nSiO_2$.

n	100° 9 days	125° 10 days	150° 8 days	200° 5 days	225° 4 days	250° 7 days	300° 3 days
1	U	U	U	Fair A Fair V V. poor T?	Fair A Fair V	Fair A Fair V	Fair A Fair V
2	Poor R	Poor R	Poor R	Good V	Good V	Good V	Good V
3	Poor R	Poor R	Poor Q	Good V V. poor T?	Good V Poor T	Fair V Fair T Poor L	Good V Poor L
4	Poor R Poor Q	Poor R Poor Q	Poor Q	Good V V. poor T?	Good V Poor T	Fair V Poor T Poor L	Good V
5	Poor Q	Poor Q	Poor Q	Good V V. poor T?	Good V Poor T	Fair V Poor T Poor L	Good V
6	Poor Q	Poor Q	Poor Q	Good V V. good T	Good V V. poor T	Fair V Poor T Poor L	Good V
7	U	U	Poor Q	Good V V. poor T	Good V	Fair V Poor T Poor L	Good V
8	U	U	U	Good V V. poor T	Good V	Fair V Poor T Poor L	Good V
9	U	U	U	Good V	Good V	Good V	Good V

TABLE 8. *Crystallisation of* $3NH_4{\cdot}OH,Al_2O_3,2SiO_2$ *at* 300° *in aqueous methanol.*

Methanol (vol. %)	Product	Methanol (vol. %)	Product
0	N-K (mica)	33	N-V + poor N-M
6·6	N-K	60	N-V + poor N-M
13	N-V (montmorillonite type)		

Even at temperatures above 150° the gels tended to remain stable, or else the products were in fine colloidal suspension. This was particularly true when the product was, or contained, montmorillonite. The montmorillonite tended to persist as a sol which could not all be centrifuged off even after 3 or 4 hr. Thus, in a crystallisation from a gel of composition $3NMe_4{\cdot}OH,Al_2O_3,2SiO_2$ + aq. at 200° the product, montmorillonite, although obtained pure,

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was only isolated in about a 25% yield, the rest remaining in colloidal suspension. If non-thixothropic gels were used as the starting material, then bayerite was usually one of the products.

The nature of the crystalline products tended to vary with the method of mixing of the gels. Normally the organic base and alumina were first mixed and then were stirred into the silica sol. In another procedure, used in a few experiments only, water was added to the alumina gel, followed by silica sol and then by tetramethylammonium hydroxide, always while stirring. After crystallisations at 200° N-T (sodalite-type crystals) and N-V (montmorillonite) were obtained from compositions $3NMe_4{\cdot}OH,Al_2O_3,nSiO_2$ + aq. in which n = 1—3, while for n = 5—7 fair N-Q (Linde sieve A analogue) and a trace of montmorillonite were obtained. When n = 4, N-Q, N-T, and N-V were all formed. After crystallisation at 150° bayerite was found mixed with other crystalline species which were N-T for n = 2 and N-Q for n = 3 or 4. This sequence shows considerable variations on the results summarised in Table 7 for the normal method of mixing.

Hydrothermal Crystallisation of Gels in Presence of H_2O–MeOH *Mixtures.*—The hydrolysis of alkylammonium ions as indicated in eqn. 1 should be arrested or reversed in presence of methanol. Accordingly crystallisation was studied at 300° for 4 days with gels $3NH_4{\cdot}OH,Al_2O_3,2SiO_2$ and the various water–methanol mixtures of Table 8. Since montmorillonite did not crystallise from systems in which the only base present was $NH_4{\cdot}OH$, but was formed when the bases were $NMe_3H{\cdot}OH$ and $NMe_4{\cdot}OH$, the results in Table 8, lines 3—5, indicate methylation of the ammonium ion under hydrothermal conditions.

Microanalysis of the layer-lattice compound N-V crystallised from the 13% methanol–water gave a nitrogen : carbon ratio by weight of 1 : 0·56, to be compared with 1 : 0·86 for $NMeH_3^+$ ions. Thus the cations present are probably mainly ammonium and monomethylammonium. However, the total nitrogen content was 6·78%, quite near that expected for a mica, whereas the *X*-ray pattern is nearest to montmorillonite. Therefore in this one specimen there is much absorbed base or, more probably, the aluminosilicate sheets carry the charge density of mica sheets but have the turbostratic arrangement and interlayer distance of montmorillonite sheets.

The species N-M of Table 8 was not identified. The main *d*-spacings in Å, and their intensities, were: 4·13w; 3·94w; 2·57w; 2·52vw; and 2·46vw. A small amount of species N-K was also detected by electron microscopy amongst the products containing N-V.

TABLE 9. *Some* d*-spacings in* Å *of* N-T *and* N-V *and comparison with natural counterparts.*

Natural sodalite (A.S.T.M. index)			N-T		Natural montmorillonite [10]			N-V (*X*-ray)		N-V (electron diffraction)		Natural [10] beidellite	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*
6·3	17	110	6·33	s	4·5	s	11,02	4·45	vs(B)	—	—	4·45	vs
4·42	3	200	—	—	4·3			—	—	—	—	—	—
3·63	100	211	$3·64_4$	vs	—	—	—	—	—	2·83	m	—	—
2·81	5	301	$2·82_6$	mw	2·56			2·55	s(B)	2·55	s	2·60	vs
2·56	13	222	$2·58_0$	ms	2·50	s	13,20	2·46	w(B)	—	—	2·49	
2·37	17	312	—	—	—	—	—	—	—	—	—	2·38	—
2·08	33	303	$2·10_4$	w	2·20	vw	22,04	—	—	$2·21_7$	w	$2·24_0$	vw
1·98	2	402	—	—	—	—	—	—	—	—	—	$2·16_4$	
1·88	2	332	$1·90_5$	vw	—	—	—	—	—	—	—	$2·09_0$	
1·80	2	224	—	—	—	—	—	—	—	—	—	$1·89_0$	—
1·73	2	314	$1·75_0$	mw	1·69	m	31,15,24	$1·68_5$	w(B)	$1·68_9$	s(B)	$1·69_4$	m
1·61	1	215	$1·62_8$	vw	1·67			—	—	—	—	$1·65_4$	
1·56	10	404	$1·57_6$	vw	1·49	s	33,06	$1·47_5$	m(B)	$1·48_9$	m	$1·48_3$	vs
1·52	5	334	—	—	1·48			—	—	—	—	—	—
1·48	7	600	—	—	$1·28_5$	m	26,40	$1·27_5$	m(B)	$1·28_6$	m	$1·28_4$	m
1·43	8	611	—	—	$1·27_5$			—	—	—	—	—	—
1·40	1	620	—	—	$1·23_5$	w	35,17,42	$1·23_5$	m(B)	$1·24_1$	s	$1·24_1$	m
1·37	2	541	—	—									
1·33	2	622	$1·34_7$	vw									
1·31	2	631	—	—									
1·28	1	444	$1·28_6$	vw									
1·20	7	—	$1·21_4$	vw									
a = 8·88 Å			a = 8·93 Å					a_0 = 5·10 b_0 = 8·90				a_0 = 5·14 b_0 = 8·93	

Some Individual N-Aluminosilicates.—Species N-A (boehmite, Al_2O_3,H_2O) and N-C (bayerite, $Al_2O_3,3H_2O$) will not be described; they are common products from gels in which freshly prepared aluminium hydroxide is one of the constituents.[8]

Species N-T. This was a somewhat expanded form of sodalite. The cubic unit cell had $a = 8{\cdot}93$ Å (compared with 8·77—8·90 Å for natural sodalites and 8·94 Å for a basic sodalite [9]). *d*-Spacings and intensities are given in Table 9, and are compared with those of a natural sodalite. The crystals could be grown only from the gels originally containing tri- and tetramethylammonium hydroxide, and could not be obtained as sole product.

TABLE 10. d-*Spacings* (Å) *of species* N-P *and comparison with natural counterparts.*

Na-Pl [3, 5]			N-L		Na-Q [5]			N-Q		Na-R [5]			N-R	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*
7·1	s	110	$7{\cdot}0_9$	vs	12·36	vs	100	12·1	s	14·52	vs	111	—	—
—	—	—	$[6{\cdot}6_9$	w]	8·77	s	110	8·60	s	8·84	ms	220	8·80	vs
5·0	m	200	$5{\cdot}0_0$	ms	7·15	s	111	7·02	s	7·56	ms	311	7·51	s
4·10	s	112	$4{\cdot}0_9$	vs	6·35	w	200	6·08	vw	5·74	s	331	5·72	ms
3·45	vw	220	3·54	w	5·52	s	210	5·44	w	4·81	m	511	4·80	m
—	—	221	3·34	vw	5·02	w	211	4·97	w	4·42	ms	440	4·41	ms
3·18	vvs	310	3·17	vs	4·36	m	220	4·30	mw	4·20	vvw	531	4·27	mw
2·90	vw	222	—	—	$4{\cdot}10_2$	s	300	4·05	vs	$3{\cdot}95_4$	w	620	3·93	m
2·68	s	321	$2{\cdot}67_7$	s	$3{\cdot}89_9$	w	310	$3{\cdot}83_3$	mw	$3{\cdot}81_3$	ms	533	—	—
2·52	vw	400	$2{\cdot}51_1$	w	$3{\cdot}71_3$	s	311	$3{\cdot}65_9$	vs	$3{\cdot}76_9$	mw	622	3·79	vs
2·41	vw	410,322	—	—	$3{\cdot}41_3$	m	320	$3{\cdot}36_5$	ms	$3{\cdot}62_1$	vvw	444	—	—
2·36	w	411,330	—	—	$3{\cdot}28_7$	ms	321	$3{\cdot}24_3$	s	$3{\cdot}51_5$	vvw	551	$3{\cdot}48_4$	vw
2·23	vw	204	$2{\cdot}23_9$	vw	$3{\cdot}07_2$	vw	400	—	—	—	—	642	$3{\cdot}32_2$	vs
			$2{\cdot}13_6$	w	$2{\cdot}98_2$	vs	410	$2{\cdot}94_1$	s	—	—	731	$3{\cdot}24_0$	vw
			$2{\cdot}04_7$	vw	$2{\cdot}90_0$	m	411	$2{\cdot}85_6$	m	$3{\cdot}08_4$	m	733	$3{\cdot}03_8$	m
			$1{\cdot}96_2$	m	$2{\cdot}75_1$	m	420	$2{\cdot}71_2$	mw	$2{\cdot}94_1$	m	660	$2{\cdot}93_1$	mw
			$1{\cdot}82_9$	vw	$2{\cdot}68_1$	mw	421	$2{\cdot}64_6$	mw	$2{\cdot}88_1$	s	555	$2{\cdot}86_7$	s
			$1{\cdot}77_2$	mw	$2{\cdot}62_3$	s	332	$2{\cdot}58_5$	ms	$2{\cdot}79_0$	m	480	$2{\cdot}77_9$	m
			$1{\cdot}71_7$	m	$2{\cdot}51_2$	mw	422	$2{\cdot}47_9$	w	$2{\cdot}74_5$	w	753	$2{\cdot}73_0$	vw
			$1{\cdot}66_9$	mw	—	—	500	$2{\cdot}42_9$	w	$2{\cdot}72_5$	vw	842	—	—
			$1{\cdot}62_4$	w	$2{\cdot}36_9$	mw	511	—	—	$2{\cdot}66_2$	m	664	$2{\cdot}64_8$	m
			$1{\cdot}47_9$	mw	$2{\cdot}24_7$	w	521	$2{\cdot}21_5$	mw	$2{\cdot}61_7$	mw	931	$2{\cdot}60_7$	vw
			$1{\cdot}39_0$	w	$2{\cdot}17_4$	m	440	$2{\cdot}14_4$	m	$2{\cdot}54_5$	mw	844	$2{\cdot}53_8$	w
			$1{\cdot}36_3$	mw	$2{\cdot}14_5$	mw	441	—	—	$2{\cdot}40_3$	m	1022	$2{\cdot}39_2$	m
			$1{\cdot}31_3$	vw	$2{\cdot}10_9$	mw	433	—	—	—	—	1040	$2{\cdot}30_8$	vw
			$1{\cdot}27_1$	mw	$2{\cdot}07_8$	mw	531	—	—	$2{\cdot}20_6$	m	880	$2{\cdot}19_6$	w
					$2{\cdot}05_0$	m	600	$2{\cdot}02_4$	m	$2{\cdot}18_1$	m	955	$2{\cdot}17_0$	w
$a = 10{\cdot}0_1$ Å			$a = 10{\cdot}02$ Å		$a = 12{\cdot}30$ Å			$a = 12{\cdot}13$ Å		$a = 24{\cdot}96$ Å			$a = 24{\cdot}85$ Å	

Species N-V (*alkylammonium montmorillonites*). The unit cell dimensions of a specimen of tetramethylammonium montmorillonite were $a = 5{\cdot}10$, $b = 8{\cdot}90$, and $c = 11{\cdot}6$ Å. The *d*-spacings are given in Table 9, where they are compared with those of natural montmorillonite and beidellite. The *c*-spacing of N-V varies, in the same way as that of natural montmorillonites, according to the inter-layer cation. The *c*-spacings for samples of N-V crystallised at different temperatures are shown in Fig. 7 as a function of these temperatures. At 200° the *c*-spacing corresponded to that of tetramethylammonium montmorillonite prepared from the natural clay, while at 300° it corresponded to that of the monomethylammonium form,[11] in both cases for products crystallised from gels originally containing only tetramethylammonium cations. This variation in cations present, when one original base was used, can be ascribed to hydrolysis of the organic bases. Microanalysis of the crystals confirmed that the cation mainly present was that indicated by the measurement of the *c*-spacing. Thus the product crystallised at 200° from the gel $3NMe_4{\cdot}OH,Al_2O_3,SiO_2$ gave C 6·55, H 3·20, and N 1·96%, the C : N ratio being 3·29 compared with 3·43 for the NMe_4^+ ion.

Crystals of species N-V were obtained free from other species, but were prepared only from gels containing originally NMe_3H^+ and NMe_4^+ ions. The thermograms and the thermogravimetric curves of tetramethylammonium-V are shown in Figs. 1*d* and 8*a*. There are

[8] Barrer and White, *J.*, 1951, 1167.
[9] Barrer and White, *J.*, 1952, 1561.
[10] Cf. McEwan, "X-ray Identification and Structure of Clay Minerals," Min. Soc., G.B., 1951, Chap. IV.
[11] Reay, Ph.D. Thesis, London, 1956.

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exothermal peaks at 333°, 396°, and 590° on the thermogram which are characteristic of the pyrolysis of the organic ions.[12] The endothermic peak at 120° is associated with the loss of interlayer water. The thermogram and thermogravimetric curves of monomethylammonium-V (prepared from $3NH_4{\cdot}OH,4Al_2O_3,2SiO_2$ + aq. + 13% of methanol) are also shown in Figs. 1*c* and 8*b*. On the thermogram one exothermal peak with a maximum at 427° was observed. Endotherms with peaks at 500° and 580° are characteristic of the loss of structural water from montmorillonites. In NMe_4-V these peaks are smothered by the exothermal pyrolysis peaks. The essential lattice structure of N-V was stable to ~900°. After being heated to this temperature the material had unit cell dimensions $a = 5{\cdot}14$, $b = 9{\cdot}00$, and $c \approx 9{\cdot}6$ Å. In the thermogram of NMe_3-V, a sharp exothermic peak at 980°, preceded by a small endothermic peak, marks the partial recrystallisation to mullite. The NH_3Me-V also recrystallises to mullite below 1050° although without an exothermal peak.

An electron micrograph and diffraction pattern of N-V are shown in Plates 1*c* and *d*. The heat of interlayer water loss from NH_3Me-V (peak temperature 70°) was estimated from the

FIG. 7. *c-Spacings of nitrogenous montmorillonites crystallised at various temperatures from tetramethylammonium* (×) *and trimethylammonium aluminosilicate gels* (○). *On the right of the diagram the arrows are drawn at c-spacings observed for the indicated methylammonium ion-exchanged montmorillonites, prepared from natural montmorillonites.*[11]

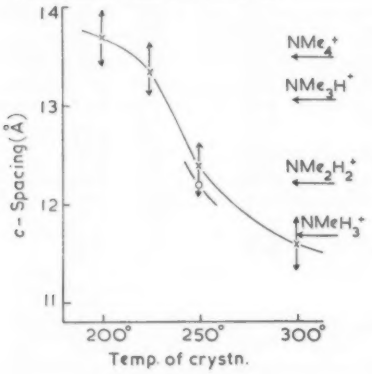
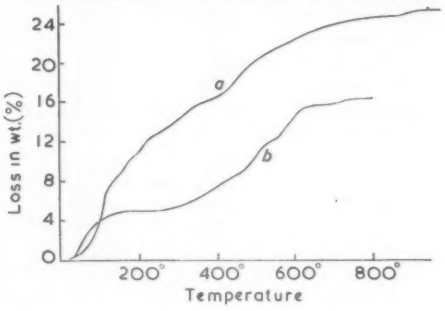


FIG. 8. *Thermogravimetric curves of synthetic tetramethylammonium montmorillonites* (*curve a*) *and monomethylammonium montmorillonite* (*curve b*).



thermogram and thermogravimetric curve, after calibration of the differential thermal analyser,[3] 24·8 kcal. per mole of water lost.

Species N-L. This is the cubic variety of harmotome which was obtained from certain alkylmmonium aluminosilicate gels in almost 100% yield (Tables 5 and 6). It is analogous to the zeolite Na-Pl which served to determine the essential structure of the aluminosilicate framework of the harmotome–phillipsite zeolites.[3] The best yields were obtained from aqueous gels $3NH_2Me_2{\cdot}OH,Al_2O_3,nSiO_2$ ($2 \leqslant n \leqslant 6$) at 200°. The unit cell edge was 10·02 Å and did not vary in products grown from gels of different compositions and at different temperatures. The *d*-spacings are compared with those of Na-Pl in Table 10.

Microanalysis of a specimen crystallised at 200° from the above gel with $n = 3$ gave N 3·97, C 5·32, and H 2·84%. The C : N ratio is 1·34, compared with C : N = 1·71 for $NH_2Me_2^+$ and 0·86 for NH_3Me^+, so that dimethylammonium ions predominate slightly in this structure. The thermogram of a sample of N-L is shown in Fig. 9 and the thermogravimetric curve in Fig. 2 (*b*). The large exotherm with its peak at 475° is associated with pyrolysis of the organic ions. The endotherm with its peak at 88° is associated with loss of zeolitic water. At 850° an amorphous phase appears (admixed with carbon) which persists at least to 1050°. The

[12] Allaway, *Proc. Soil Sci. Soc. Amer.*, 1948, **13**, 183.

photomicrograph of N-L, and the electron diffraction pattern, are shown in Plates 1*e* and *f*. The *d*-spacings derived from this pattern agreed with the *X*-ray *d*-spacings of Table 10.

Species N-Q. This was the nitrogenous analogue of Na-Q,[5] and therefore of Linde molecular sieve A. It was obtained pure but in low yield, and by microanalysis it was established that the cation mainly present in the sample analysed was $NH_2Me_2^+$. Thus, the C : N ratio was 1·89, to be compared with 1·71 for $NH_2Me_2^+$ and 2·57 for $NHMe_3^+$. Species N-Q crystallised only from tetramethylammonium aluminosilicate gels and the low yield may be governed by the rate of hydrolysis of NMe_4^+ which must be very slow at the low temperatures (~100—150°) at which it was obtained. The *d*-spacings are compared with those of Na-Q in Table 10, and a photomicrograph is shown in Plate 2*a*.

Species N-R. This was identified as an alkylammonium analogue of faujasite, and hence of Na-R [5] and Linde sieve X. As with N-Q it was obtained pure but in low yield. Microanalysis of a particular sample gave a C : N ratio of 1 : 3·44, to be compared with 3·43 for

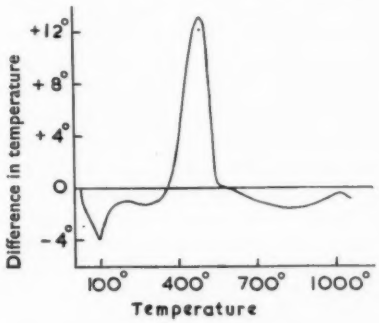


FIG. 9. *Thermogram of nitrogenous harmotome from* $3NMe_2H_2{\cdot}OH,Al_2O_3,3SiO_2 + aq.$ *at* 200°.

NMe_4^+. This ion should therefore be the only organic cation present. The cavities and channels in faujasite are filled by about 33 CMe_4 molecules per unit cell; [13] a comparable number of NMe_4^+ ions might therefore also fill this structure. This corresponds to a silica-rich aluminosilicate framework, which would therefore be the only possible form of faujasite structure containing only tetramethylammonium ions.

The *d*-spacings of species N-R are given in Table 10, in which they are compared with those of Na-R.[5] The cubic unit cell edge is 24·85 Å. Plates 2*b* and *c* show a photomicrograph and the electron diffraction pattern of N-R. The *d*-spacings so determined agreed well with those obtained by *X*-ray diffraction. The material is excellently crystalline.

DISCUSSION

Ease of Crystallisation.—The ease of crystallisation varied greatly from one base to another. Crystallisation was, for instance, observed down to 150° in the dimethylammonium aluminosilicate system, but only down to 250° in the ammonium aluminosilicate system. If the basic dissociation constants are estimated at the minimum crystallisation temperatures by means of Pitzer's equation [14] there is a correlation between them, as shown in Table 11.

Appearance of Layer Lattices.—In hydrothermal systems the crystallisation of layer-lattice species related to montmorillonite, beidellite, and other clay minerals, occurs from alkali-metal aluminosilicates only when the amount of alkali-metal base is limited or, for kaolinites, virtually absent.[15] The framework minerals (*e.g.*, zeolites, felspars, felspathoids) replace layer-lattice minerals when the amount of alkali is increased and particularly when it is in excess. However, among the ammonium and methylammonium

[13] Barrer and Sutherland, *Proc. Roy. Soc.*, 1956, **237***A*, 439.
[14] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.
[15] Norton, *Amer. Mineral.*, 1939, **24**, 1; Ewell and Insley, *J. Res. Nat. Bur. Stand.*, 1935, **15**, 173; Roy and Sand, *Amer. Mineral.*, 1956, **41**, 505.

aluminosilicates we have shown not only that diverse framework structures can be formed, but that, even in presence of excess of base, layer-lattice species are formed very readily and can become the dominant crystalline phases. With smaller ions, notably in the case of NH_4^+, the important layer structure is a mica; as the ions increase in size, micas are replaced by montmorillonite-type clays. The tendency to form layer lattices is thus very differently manifested by the organic bases and by alkali-metal hydroxides.

TABLE 11. *Basic dissociation constants and minimum crystallisation temperatures, T_m.*

Base	T_m	Basic dissocn. const. at T_m	Base	T_m	Basic dissocn. const. at T_m
NH_4OH	~250	$1{\cdot}9_5 \times 10^{-6}$	$NH_2Me_2{\cdot}OH$	~150	$8{\cdot}5 \times 10^{-5}$
$NHMe_3{\cdot}OH$.....	~230	$4{\cdot}9 \times 10^{-6}$	$NMe_4{\cdot}OH$	~100	Strong base
$NH_3Me{\cdot}OH$	~210	$2{\cdot}0 \times 10^{-5}$			

The number of cations between the lamellæ in a montmorillonite having the ion-exchange capacity of Ross and Hendricks's ideal formula [16] is sufficiently low to be able to accommodate any methylammonium ion.[17] On the other hand, the cation density for micas of normal composition allows an area of only 23·4 Å^2 per ion. The areas of several alkylammonium ions have been estimated [11] as follows: NMe_4^+ 26 Å^2; NMe_3H^+ 26 Å^2; $NMe_2H_2^+$ 24 Å^2; $NMeH_3^+$ 17 Å^2. Therefore, of these ions, only ammonium, methylammonium (and possibly $NMe_2H_2^+$) could form micas having normal cationic compositions. Also, in mica the sheets do not expand readily and so the height of the ions may be important. The spherical ammonium ion, of similar diameter (2·86 Å) to K^+ (2·66 Å), should and evidently does form a stable mica structure. There is, however, difficulty when $NMeH_3^+$ is to be incorporated. The full cation density in mica has been realised in one preparation (p. 978) in which, however, the crystals were more like montmorillonite in the diffuseness of the *X*-ray pattern. This species represents an interesting intermediate phase. Finally, in accordance with the areas of the alkylammonium ions, layer-lattices rich in di-, tri-, and tetra-methylammonium ions were montmorillonoids in *c*-spacings (Fig. 7) and, from microanalysis for nitrogen, in cation density.

The Zeolites.—Among the various zeolitic phases the same problem arises of finding adequate intracrystalline space for packing in the number of alkylammonium ions needed to neutralise the framework charges. This difficulty has been commented upon in relation to N-R (faujasite). It arises equally in the cases of N-Q, N-T, and N-L. The possibility of incorporation only of small hydrolysis products (*e.g.*, NH_4^+ or $NMeH_3^+$ from NMe_4^+) is not fully supported by the microanalyses. It may be surmised that these zeolites tend to be silica-rich relative to their analogues containing only simple inorganic cations, although no proof of this can be offered. Alternatively, hydrogen ions may be incorporated along with larger alkylammonium ions. Species N-L (harmotome), for example, crystallised very readily from gels with $NMe_2H_2{\cdot}OH$ as base, and analysis showed much dimethylammonium ion to be present. However, the nitrogen content (3·97%) corresponds with a highly siliceous phase unless H_3O^+ is also present. The same is true of N-Q (4·2% N) and N-R (2·0% N).

The electron-microscopy and electron-diffraction studies reported in this and the following paper were carried out by Dr. I. S. Kerr of this Department, whom the authors thank.

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[*Received, June 2nd,* 1960.]

[16] Ross and Hendricks, U.S. Geol. Survey, Prof. Paper 205B, 1945.
[17] Barrer and Reay, *Trans. Faraday Soc.*, 1955, **51**, 1290.

202. *Hydrothermal Chemistry of the Silicates. Part X.* A Partial Study of the Field* $CaO–Al_2O_3–SiO_2–H_2O$.

By R. M. Barrer and P. J Denny.

A hydrothermal study has been made of part of the $CaO–Al_2O_3–SiO_2–H_2O$ system in the range 125—450°. The crystalline products depended to some extent upon whether the silica was introduced as a sol or as powdered silica glass. These products included boehmite, corundum, and two calcium aluminate hydrates as silica-free species; and cristobalite, and small amounts of wollastonite and foshagite, as alumina-free species. A series of grossularite-hydrogarnets was prepared, and also a number of zeolites (tetragonal and cubic analcites, thomsonite, harmotome, epistilbite, and a little mordenite). Anhydrous phases formed included anorthite and its hexagonal dimorph. By sintering reactions the hydrated phases were transformed for the most part into anorthite, its hexagonal dimorph, and $12CaO,7Al_2O_3$. A number of the phases have been characterised by thermogravimetry, differential thermal analysis, *X*-ray diffraction, and electron and optical microscopy; and crystallisation fields have been delineated. Crystallisation is normally less complete than for alkali-metal aluminosilicates under comparable conditions. Addition of tetramethylammonium hydroxide to the calcium aluminosilicate gels resulted in the appearance of bayerite, a sodalite-type structure, a zeolite of the gmelinite-chabazite family, and a montmorillonoid as additional phases.

Of the various calcium silicates a number have been synthesised by hydrothermal methods,[1] and the majority have been characterised by *X*-ray and optical methods.[2] Aluminates of calcium have also received attention [3] and have been produced hydrothermally together with hydrated forms of alumina such as gibbsite and boehmite. The system $CaO–Al_2O_3–SiO_2–H_2O$ has been examined in part by various workers. Goldsmith and Ehlers [4] crystallised compositions $CaO,Al_2O_3,2SiO_2$ + aq. over the temperature range 220—504°, with glasses and oxide mixtures as starting materials. Anorthite, a hexagonal dimorph of this felspar, and the fibrous zeolite thomsonite were reported. Ehlers [5] also prepared thomsonite, and at higher temperatures grossularite, anorthite, and its hexagonal dimorph, the parent mixtures of oxides and of glass being of composition $4CaO,3Al_2O_3,6SiO_2$. Davis and Tuttle [6] made anorthite and its hexagonal and orthorhombic polymorphs by the pyrolytic method.

Ames and Sand [7] recently synthesised the zeolites calcium analcite (wairakite) and calcium mordenite from co-precipitated gels and calcined nitrates. The wairakite was formed from mixtures of composition $CaO,Al_2O_3,5SiO_2$ + aq. Mordenite was prepared from hydrous mixtures $CaO,Al_2O_3,10SiO_2$ (at 340—380°/1000 atm.), and at 455° anorthite and cristobalite were found as crystalline products. Ellis [8] also studied the hydrothermal crystallisation of calcium aluminosilicate glasses and oxide mixtures of composition $CaO,Al_2O_3,8SiO_2$ between 200° and 450°. From glasses, quartz, anorthite, epistilbite, analcite, mordenite, and heulandite were reported, but from oxide mixtures only cristobalite, anorthite, analcite, and mordenite. Using glass of composition $3CaO,Al_2O_3,nSiO_2$

* Part IX, preceding paper.

[1] See *e.g.*, Corwin, Yalman, Edwards, and Shaw, *J. Phys. Chem.*, 1957, **61**, 941; Assarsson, *J. Phys. Chem.*, 1958, **62**, 223; Heller and Taylor, *J.*, 1951, 2397; Taylor, *J.*, 1953, 163.

[2] Heller and Taylor, "Crystallographic Data for the Calcium Silicates," D.S.I.R. and H.M.S.O., London, 1956.

[3] *E.g.*, Majumdar and Roy, *J. Amer. Ceram. Soc.*, 1956, **39**, 434; Schneider and Thorvaldson, *Canad. J. Res.*, 1941, **19**, *B*, 123; Johnson and Schneider, *ibid.*, 1943, **21**, *B*, 236.

[4] Goldsmith and Ehlers, *J. Geol.*, 1952, **60**, 386.

[5] Ehlers, *J. Geol.*, 1953, **61**, 233.

[6] Davis and Tuttle, *Amer. J. Sci.*, Bowen Vol., 1952, p. 107.

[7] Ames and Sand, *Amer. Mineral.*, 1958, **43**, 476.

[8] Ellis, Ph.D. Thesis, Otago, N.Z.

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($n = 1$—3), Flint, McMurdie, and Wells [9] made members of the hydrogrossular series, which were solid solutions of composition intermediate between the end-members $3CaO,Al_2O_3,6H_2O$ and $3CaO,Al_2O_3,3SiO_2$, but the anhydrous end-member $3CaO,Al_2O_3,3SiO_2$ could not be synthesised. Stability relations of hydrogrossulars were also examined by Yoder.[10]

The CaO–Al_2O_3–SiO_2–H_2O system continues to attract attention [11] on account of its importance both geologically and technically, but even so exploration has been partial only, and it appears that the products often depend on the nature of the starting materials.[8] It was, therefore, of considerable interest to examine this system further, especially with active hydrous aluminosilicate gels as reactants. In the sodium aluminosilicate field crystallisation from active gels can occur at 100° or below; [12] but less reactive materials crystallise only above about 150°.[13] The crystalline products then vary according to the temperature of growth. In the present paper we record the results of a further partial exploration of the lime–alumina–silica–water system, in which the reactivity of the starting materials is varied, and in which additional chemical aspects of crystallisation have been examined.

Experimental

Two forms of silica were used: "Syton 2X," a stable sol containing 30% by weight of silica; and finely powdered "Vitreosil" silica glass, of purity greater than 99·8%. The alumina was a freshly prepared amorphous gel, made as described elsewhere.[14] The calcium oxide was obtained by ignition of finely powdered "AnalaR" calcium carbonate. When silica sol was used, the gels were made by first grinding solid calcium oxide and alumina gel together. Distilled water was added and the suspension stirred. "Syton 2X" was then added and the mixture stirred for a further 15 min. With silica glass as a starting material the three components were mixed in the correct proportions and ground while dry. The charge was placed in the autoclave, and distilled water was added.

Stainless-steel autoclaves of about 16 c.c. internal capacity were employed as reaction vessels. Preparations on a larger scale were made in an electrically heated 1 l. autoclave supplied by C. W. Cook and Sons Ltd. In all syntheses the ratio of water to solid was near 10 c.c. per 0·75 g. The degree of filling was always 0·5. Electrically heated ovens, thermostatically controlled within $\pm 1°$, were used for heating up to 300° c, and an electrically heated furnace for heating between 300° and 450°. The furnace could hold nine autoclaves simultaneously and was maintained at constant temperature within $\pm 2°$. Seven chromel–alumel thermocouples were placed at different points of the copper heating-block to check that no appreciable thermal gradients appeared.

After the appropriate heating period the autoclaves were air-cooled or water-quenched. The pH's of the cold mother-liquors were measured, and the products were then filtered or centrifuged off and washed with distilled water until neutral to indicators. They were then air-dried, or dried in an oven at 75°, or in a vacuum-desiccator. The white powders were then examined by *X*-ray diffraction, optically, by electron microscopy and electron diffraction, and by differential thermal analysis and thermogravimetry.

In *X*-ray work, a Guinier camera, and also a 9 cm. Debye–Scherrer powder camera, were variously used, with filtered Cu-K_α radiation, supplied either by a Raymax *X*-ray diffraction unit or by a Hilger HRX *X*-ray unit. A Leitz polarising microscope and a Vickers projection microscope were employed in optical work, and a Philips electron microscope for the further examination of the crystals. The differential thermal analyser and thermogravimetric equipment have been described elsewhere.[15] The rate of heating in both differential thermal analysis and thermogravimetry was 10° per min.

[9] Flint, McMurdie, and Wells, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 13.
[10] Yoder, *J. Geol.*, 1950, **58**, 221.
[11] Glasser and Roy, *Amer. Mineral.*, 1959, **44**, 447; Roy, *J. Amer. Ceram. Soc.*, 1958, **41**, 293.
[12] Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.
[13] Barrer and White, *J.*, 1951, 1167.
[14] *E.g.*, Weiser and Milligan, *J. Phys. Chem.*, 1937, **41**, 1029.
[15] Barrer and Langley, *J.*, 1958, 3804.

Results

Although the calcium aluminosilicate gels did not crystallise as readily as did those of the alkali metals it was possible to obtain major or minor yields of the species given in Table 1. The ease of crystallisation diminished with falling temperature, and as the silica content increased relative to the amount of alumina and base. Rather surprisingly, the reactive gels prepared from " Syton 2X " silica sols often crystallised less readily than did mixtures containing powdered silica glass. This behaviour may be attributed to the large surface of the reactive gels, which adsorbed calcium hydroxide strongly [18] and so lowered the pH of the mother-liquor and reduced the solubility of the gel, which is always higher in alkaline media. Attempts to saturate the crystallising gels with calcium by adding calcium chloride to the mother-liquors

Table 1. *Crystalline species formed from calcium aluminosilicate gels and mixtures.*

Reference letter	Identification	Maximum yield *
Ca-A	Boehmite, Al_2O_3,H_2O	Major
Ca-B	Corundum, Al_2O_3	Major
Ca-M	$4CaO,3Al_2O_3,3H_2O$	Major
Ca-D	Tetragonal Ca-analcite, $CaO,Al_2O_3,4SiO_2,2H_2O$	Major
Ca-E	Cubic Ca-analcite, $CaO,Al_2O_3,4SiO_2,2H_2O$	Major
Ca-F	Anorthite, $CaO,Al_2O_3,2SiO_2$	Major
Ca-P	Hexagonal dimorph of anorthite, $CaO,Al_2O_3,2SiO_2$	Major
Ca-H	α-Cristobalite, SiO_2	Major
Ca-I	Ca-thomsonite, $CaO,Al_2O_3,2SiO_2,2H_2O$	Minor
Ca-J	Ca-epistilbite, $CaO,Al_2O_3,6SiO_2,5H_2O$	Major
Ca-K	Hydrogrossular series, $3CaO,Al_2O_3,6H_2O$ to $3CaO,Al_2O_3,3SiO_2$	Major
Ca-L	Ca-harmotome, $CaO,Al_2O_3,3SiO_2,5H_2O$	Major
Ca-N	Tricalcium aluminate hexahydrate, $3CaO,Al_2O_3,6H_2O$	Major
Ca-O	Unidentified	Major
Ca-Q	Ca-mordenite, $CaO,Al_2O_3,10SiO_2,6{\cdot}7H_2O$	Very minor
Ca-R	Foshagite, $4CaO,3SiO_2,H_2O$	Very minor
Ca-S	Wollastonite, CaO,SiO_2	Very minor
Ca-X	Unidentified	Very minor
Ca-Y	Unidentified	Very minor
Ca-Z	Unidentified	Very minor

* A " major " yield is one in which a crystalline product appears more abundant than any other species, or gel, under microscopic examination.

Table 2. *Syntheses in the lime–alumina system.*

Anhyd. gel composition (oxide formula)	Time (days)	Temp.	Products	pH of cold mother-liquor
CaO,Al_2O_3	18	300°	Ca-A + Ca-M	>10·5
CaO,Al_2O_3	18	425	Ca-B + Ca-M	9·2
CaO,Al_2O_3	2	445	Ca-B + Ca-M	>10·5
$3CaO,Al_2O_3$	26	125	Ca-N	>10·5
$3CaO,Al_2O_3$	9	200	Ca-N + $Ca(OH)_2$ (?)	>10·5
$3CaO,Al_2O_3$	9	220	Ca-M + $Ca(OH)_2$	>10·5
$3CaO,Al_2O_3$	18	300	Ca-M	>10·5
$3CaO,Al_2O_3$	3	410	Ca-M + $Ca(OH)_2$	>10·5
$3CaO,Al_2O_3$	18	430	Ca-M	>10·5

resulted in no noticeable improvement. The products frequently contained proportions of non-crystalline gel, or were non-crystalline altogether, even after long reaction times. Where partial crystallisation had occurred several species often appeared together.

Lime–alumina gels free from silica crystallised more readily than calcium aluminosilicate gels, a behaviour ascribed to the higher pH's of the mother-liquors (compare Table 2 with Tables 3—5). At the silica-rich end crystallisation was always more sluggish still. For the formation of calcium silicates a higher lime content would be desirable.

The Lime–Alumina System.—The lime–alumina system under hydrothermal conditions yielded the products shown in Table 2. Crystalline calcium hydroxide was often a product from the lime-rich compositions, and Ca-M ($4CaO,3Al_2O_3,3H_2O$) was universally present in

[18] Greenberg, *J. Phys. Chem.*, 1956, **60**, 325.

TABLE 3. *Hydrothermal crystallisation of gels* $CaO,Al_2O_3,nSiO_2$ *prepared by using* SiO_2 *sol.*

	Temp. and times (days)							
	180°	200°	225°	245°	252°	260°	280°	285°
n	8	10—30	41	34	11	29	39	8
1	Fair Ca-M	Poor Ca-P Poor Ca-A	Fair Ca-P Fair Ca-I	Fair Ca-P Fair Ca-I	Good Ca-P	Good Ca-F Poor Ca-A	Fair Ca-P V. poor Ca-P Fair Ca-A	Fair Ca-M
	(8·9) *	(9·8)	(7·6)	(6·8)	(10·0)	(8·5)	(6·8)	(8·9)
2	Fair Ca-M	U †	U	Fair Ca-P Fair Ca-I	Good Ca-P	Good Ca-F Poor Ca-M	Good Ca-F Poor Ca-P	Fair Ca-D Poor Ca-M
	(9·6)	(7·9)	(10·0)	(6·7)	(10·5)	(5·8)	(6·4)	(9·6)
3	Fair Ca-M	U	U	U	Fair Ca-L	Fair Ca-D Fair Ca-F	Good Ca-D V. poor Ca-P	Fair Ca-M
	(7·3)	(8·0)	(10·0)	(10·0)	(6·5)	(5·6)	(6·2)	(7·3)
4	Fair Ca-M	U	Poor Ca-J	Fair Ca-J	Fair Ca-L	Good Ca-D	Fair Ca-D	Fair Ca-M
	(8·5)	(8·5)	(6·2)	(6·8)	(9·0)	(5·6)	(6·0)	(8·5)
5	Poor Ca-M	U	U	Fair Ca-J	U	Fair Ca-J	U	Fair Ca-M
	(6·9)	(8·5)	(7·3)	(8·5)	(6·6)	(5·8)	(5·6)	(6·9)
6	Poor Ca-M	U	U	Fair Ca-J	U	U	U	Fair Ca-M
	(6·9)	(8·5)	(7·4)	(6·5)	(6·5)	(5·8)	(5·5)	(6·9)
7	Poor Ca-M	U	U	U	U	U	U	Fair Ca-M
	(6·8)	(8·0)	(7·4)	(9·0)	(6·5)	(5·8)	(7·0)	(6·8)
8	Fair Ca-M	U	—	U	U	U	U	Poor Ca-M
	(8·5)			(6·6)	(6·5)	(5·8)	(5·6)	(8·5)
9	Fair Ca-M	U	—	U	U	U	U	Poor Ca-M
	(8·7)			(6·8)	(6·5)	(5·8)	(5·6)	(8·7)

	Temp. and times (days)						
	300°	351°	390°	410°	425°	440°	450°
n	32	12	8	3	3	5	6
1	Fair Ca-A Fair Ca-P Poor Ca-F	Good Ca-F Fair Ca-P Fair Ca-A	Fair Ca-A Fair Ca-F Fair Ca-P	Good Ca-F Fair Ca-P Fair Ca-A	Fair Ca-A Fair Ca-F Poor Ca-P	Good Ca-B Poor Ca-F V. poor Ca-P	Good Ca-B Poor Ca-F V. poor Ca-P
	(10·0)	(5·6)	(6·8)	(6·7)	(7·0)	(6·5)	(6·7)
2	Fair Ca-P Fair Ca-F	Good Ca-F Poor Ca-P	Good Ca-F Fair Ca-P	Good Ca-F Fair Ca-P Poor Ca-E V. poor Ca-A	Good Ca-F Fair Ca-P Poor Ca-A	Good Ca-F Fair Ca-A Fair Ca-P	Good Ca-F Poor Ca-P
	(10·5)	(5·6)	(5·7)	(5·7)	(6·5)	(6·0)	(6·5)
3	Good Ca-D Poor Ca-F V. poor Ca-P	Fair Ca-F Fair Ca-E Poor Ca-P	Good Ca-E Poor Ca-F Poor Ca-P	Good Ca-E Poor Ca-F Poor Ca-P	Good Ca-F Poor Ca-P V. poor Ca-E	Good Ca-F Fair Ca-P	Fair Ca-F Fair Ca-P Poor Ca-H
	(6·5)	(5·6)	(5·5)	(5·6)	(5·7)	(5·4)	(6·0)
4	Good Ca-D Poor Ca-F	Good Ca-E Poor Ca-F V. poor Ca-P	Good Ca-E Poor Ca-F Poor Ca-P	Fair Ca-E V. poor Ca-F V. poor Ca-P	Fair Ca-E Fair Ca-F Poor Ca-P	Fair Ca-E Fair Ca-F Poor Ca-P	Fair Ca-F Fair Ca-P Fair Ca-H
	(9·0)	(5·5)	(5·4)	(10·5)	(5·5)	(5·5)	(5·4)
5	U	Good Ca-E V. poor Ca-F	Good Ca-E Poor Ca-F Poor Ca-P	Poor Ca-F	Good Ca-E Poor Ca-F Poor Ca-P	Good Ca-E Fair Ca-F Poor Ca-P	Fair Ca-F Fair Ca-P Fair Ca-H
	(6·6)	(5·6)	(5·5)	(5·7)	(5·7)	(5·5)	(5·5)
6	U	Poor Ca-E	Good Ca-E V. poor Ca-F Poor Ca-P	V. poor Ca-E	Poor Ca-H V. poor Ca-F	Fair Ca-F Poor Ca-P Fair Ca-H	U
	(6·5)	(5·5)	(5·5)	(5·7)	(5·7)	(5·5)	(7·2)
7	U	U	Good Ca-E V. poor Ca-F Poor Ca-P	U	U	Fair Ca-F Poor Ca-P Fair Ca-H	Good Ca-H Poor Ca-P Poor Ca-F
	(6·5)	(5·5)	(5·7)	(5·7)	(5·7)	(5·5)	
8	U	U	Good Ca-E V. poor Ca-F V. poor Ca-P	U	U	Good Ca-H Poor Ca-P V. poor Ca-F	Good Ca-H Poor Ca-P Poor Ca-F
	(6·5)	(7·9)	(5·5)	(10·5)	(5·5)	(5·5)	(5·5)
9	U	U	Good Ca-E V. poor Ca-F V. poor Ca-P	U	U	Good Ca-H Poor Ca-P V. poor Ca-F	Good Ca-H Poor Ca-P Poor Ca-F
	(6·5)	(5·5)	(5·5)	(10·0)	(5·5)	(5·5)	(5·5)

* Figures in brackets are the pH's of the cold mother-liquors after reaction.

† U denotes non-crystalline. The terms "poor," "fair," and "good" in this and similar Tables refer to the yields of the crystals. Yields were estimated visually, and from the intensities of the *X*-ray diffraction patterns.

TABLE 4. *Hydrothermal crystallisation of gels* $3CaO,Al_2O_3,nSiO_2$ *prepared by using* SiO_2 *sol.*

	Temp. and times (days)				
n	200°	220°	250°	295°	300°
	20	9	30	8	26
1	Good Ca-K(N)	Good Ca-K	Good Ca-O	Poor Ca-K	Poor Ca-O
		V. poor Ca-P		Poor Ca-O	Poor Ca-F
	(10·5) *	(7·5)	(10·5)	(10·5)	(7·6)
2	Fair Ca-K(N)	Good Ca-K	Poor Ca-O	Fair Ca-K	Fair Ca-K
		Poor Ca-P	Fair Ca-F		Poor Ca-F
	(6·9)	(8·2)	(9·8)	(8·8)	(7·2)
3	Good Ca-K(N)	Fair Ca-P	Good Ca-E	Poor Ca-K	Good Ca-F
			Poor Ca-F	Good Ca-P	+ poor ?
			V. poor Ca-O		
	(9·4)	(8·0)		(6·0)	(5·7)
4	Good Ca-K(N)	Fair Ca-P	Good Ca-E	—	Good Ca-F
			Fair Ca-F		
	(10·5)	(8·0)	(6·4)		(5·5)
5	Poor Ca-K(N)	V. poor Ca-D	Fair Ca-O	Good Ca-P	Good Ca-D
		V. poor Ca-P	Fair Ca-F	V. poor Ca-D	Poor Ca-F
	(10·0)	(5·8)	(5·8)	(5·8)	(6·0)
6	V. poor Ca-K(N)	—	Fair Ca-E	Fair Ca-O	Good Ca-D
			Poor Ca-F		V. poor Ca-F
	(6·0)		(5·8)	(5·5)	(5·6)
7	V. poor Ca-K(N)	Poor Ca-D	—	—	Good Ca-E
					Poor Ca-F
	(6·5)	(6·0)			(6·0)
8	—	U †	U	Good Ca-E	Good Ca-D
		(6·7)	(5·8)	(5·5)	(6·0)
9	—	U	U	—	U
		(6·7)	(5·5)		(6·0)

	Temp. and times (days)			
n	350°	380°	415°	450°
	10	7	6	3
1	Good Ca-O	Good Ca-O	Fair Ca-K	Good Ca-O
		V. poor Ca-K	Fair Ca-O	Poor Ca-K
	(10·5)	(10·5)	(10·5)	(10·5)
2	Good Ca-K	Good Ca-K	Good Ca-K	Good Ca-O
	Poor Ca-O	Poor Ca-O	Poor Ca-O	Poor Ca-K
	(5·0)	(8·5)	(9·4)	(8·0)
3	Fair Ca-K	Fair Ca-K	Good Ca-K	Good Ca-K
	Fair Ca-P	Fair Ca-P	V. poor Ca-O	Poor Ca-F
	(5·6)	(6·4)	(5·8)	(5·7)
4	Good Ca-P	—	Fair Ca-P	Fair Ca-F
			Fair Ca-F	Fair Ca-K
	(5·5)		(5·5)	(5·6)
5	Good Ca-E	U	Poor Ca-E	Fair Ca-F
	Poor Ca-P		Fair Ca-F	V. poor Ca-K
	(5·5)	(7·6)	(5·5)	(5·6)
6	Good Ca-E	—	Good Ca-E	—
	V. poor Ca-P		Poor Ca-F	
	(5·5)		(5·5)	
7	Good Ca-E	—	Fair Ca-O	—
	V. poor Ca-P		Poor Ca-F	
			V. poor Ca-E	
	(5·5)		(5·6)	
8	Good Ca-E	Good Ca-E	—	Poor Ca-O
	V. poor Ca-P			
	(5·5)	(5·6)		(5·5)
9	Good Ca-E	Fair Ca-O	—	V. poor Ca-O
	Poor Ca-H			
	V. poor Ca-P			
	(5·5)	(5·5)		(5·5)

* See footnotes to Table 3.

all crystalline products formed at 220° or above. At lower temperatures the more highly hydrated Ca-N ($3CaO,Al_2O_3,6H_2O$) appeared, the transition temperature Ca-N to Ca-M being between 200° and 220°. Yields were satisfactory but, especially for shorter reaction times, non-crystalline gel was often observed, and the crystals were small and irregular.

Calcium Aluminosilicate Crystallisation Fields.—The investigation was carried out by using hydrous gels of oxide formula $CaO,Al_2O_3,nSiO_2$ ($1 < n < 9$), silica sol being used to prepare the initial compositions. In a second investigation gels of oxide formula $3CaO,Al_2O_3,nSiO_2$ ($1 < n < 9$) were employed, also made with silica sol. A third study used the same compositions as the first, but with powdered silica glass as the source of silica. The experimental conditions and products are summarised in Tables 3—5.

(*a*) Species obtained from the gels $CaO,Al_2O_3,nSiO_2$ of Table 3 included mainly thomsonite, epistilbite, anorthite, its hexagonal dimorph, cristobalite, and cubic and tetragonal forms of Ca-analcite. The cubic form of analcite appeared at higher, and the tetragonal form at lower temperatures. The crystals obtained were very small and often anhedral. The growth and variety of crystals became more marked at higher temperatures and lower silica content. The reproducibility of crystal formation was found to be good, and the fields of crystal growth for several species are indicated in Figs. 1*a*, *b*, and *c*. Gels crystallised at 180° and 285° for the relatively short time of 8 days gave the calcium aluminate hydrate Ca-M as the main product for most values of *n*, but gels crystallised at similar temperatures and for longer times (about 30 days) normally failed to yield this species, which may therefore be a metastable intermediate. Calcium harmotome (Ca-L) appeared on two occasions only, after relatively shorter crystallisation times (11 days at 252°), and so may also here be metastable.

(*b*) When the more lime-rich gels $3CaO,Al_2O_3,nSiO_2$, also prepared by using silica sol, were treated hydrothermally the crystallisation times were still long (Table 4), but crystallisation proceeded more readily. Analcites again appeared over much of the field of composition, but epistilbite (Ca-J) and thomsonite (Ca-I) were absent and also cristobalite (Ca-H) was less common. Two new phases were formed, namely, Ca-O, which was not identified, and Ca-K which represented a series of grossularite hydrogarnets. The crystallisation fields are shown in Figs. 2*a*—*c*. Comparison with Fig. 1 shows that the central regions of formation of several species (Ca-E, Ca-D, Ca-P, and Ca-F) are displaced to compositions corresponding to higher silica contents. Despite the additional lime, the pH's of the cold mother-liquors (Table 4) were not noticeably above those recorded in Table 3.

TABLE 5. *Hydrothermal crystallisation of oxide mixtures* $CaO,Al_2O_3,nSiO_2$, *using powdered* SiO_2 *glass.*

	Temp. and times (days)				
n	150° 20	200° 24	250° 31	275° 18	292° 31
1	Fair Ca-N V. poor $Ca(OH)_2$ (10·5) †	V. poor Ca-N Fair Ca-L V. poor $Ca(OH)_2$ (8·5)	Poor Ca-A Poor Ca-P Poor Ca-F (10·5)	Fair Ca-A Fair Ca-P (8·7)	Poor Ca-F Fair Ca-A +? (6·7)
2	Fair Ca-N V. poor $Ca(OH)_2$ (10·5)	Fair Ca-L V. poor Ca-N V. poor $Ca(OH)_2$ (8·5)	V. poor Ca-L Poor Ca-P Poor Ca-F (6·9)	Fair Ca-F Fair Ca-P (6·0)	Fair Ca-F (6·7)
3	Fair Ca-N V. poor $Ca(OH)_2$ (8·5)	Good Ca-L V. poor $Ca(OH)_2$ (6·5)	Good Ca-L (6·7)	Poor Ca-L Poor Ca-P (6·0)	Fair Ca-E Fair Ca-F (6·7)
4	Fair Ca-N V. poor $Ca(OH)_2$ (10·5)	Good Ca-L (6·5)	Good Ca-L (6·5)	Poor Ca-P V. poor Ca-J(?) (6·0)	Good Ca-E (6·7)
5	Fair Ca-N V. poor $Ca(OH)_2$ (10·0)	Fair Ca-L V. poor $Ca(OH)_2$ (6·5)	—	V. poor Ca-J(?) Poor Ca-P (6·0)	Good Ca-E (6·7)
6	Fair Ca-N V. poor $Ca(OH)_2$ (10·0)	Poor Ca-L V. poor $Ca(OH)_2$ (6·5)	Good Ca-J (6·5)	Fair Ca-P (6·0)	Good Ca-E (6·7)
7	Poor Ca-N V. poor $Ca(OH)_2$ (10·0)	Poor Ca-L V. poor $Ca(OH)_2$ (6·5)	Good Ca-J (6·5)	Fair Ca-P (6·0)	Good Ca-E (6·7)
8	Poor Ca-N V. poor $Ca(OH)_2$ (9·5)	Fair Ca-L V. poor $Ca(OH)_2$ (6·5)	—	Fair Ca-P (6·0)	Good Ca-E (6·7)
9	Poor Ca-N V. poor $Ca(OH)_2$ (9·0)	Poor Ca-L V. poor $Ca(OH)_2$ (6·5)	—	Poor Ca-P (6·0)	Fair Ca-E (6·7)

TABLE 5. (*Continued.*)

	Temp. and times (days)				
n	300°	300°	350°	420°	450°
	5	12	7	6	4
1	—	—	Fair Ca-F	Fair Ca-F	Fair Ca-O
			Poor Ca-A	Fair Ca-P	Fair Ca-K
				V. poor Ca-A	V. poor $Ca(OH)_2$
			(9·5)	(6·7)	(6·5)
2	—	—	Good Ca-F	—	Good Ca-F
			Poor Ca-P		V. poor Ca-P
					V. poor Ca-O
					V. poor Ca(OH)
			(7·0)		(6·5)
3	Poor Ca-L	Fair Ca-L	Fair Ca-E	Fair Ca-P	Fair Ca-F
			Poor Ca-F	Fair Ca-F	Fair Ca-P
			Poor Ca-P		Fair Ca-E
					Poor Ca-H
4	(6·3)	(6·7)	(6·7)	(5·8)	(6·5)
	—	—	V. good Ca-E	—	Poor Ca-F
					Fair Ca-E
					Poor Ca-P
					Fair Ca-H
			(6·7)		(6·5)
5	—	—	Good Ca-E	Good Ca-E	Fair Ca-E
				Fair Ca-P	Poor Ca-F
				Poor Ca-F	V. poor Ca-P
					Fair Ca-H
			(6·7)	(6·0)	(6·5)
6	—	—	Fair Ca-E	Good Ca-H	Fair Ca-H
				Poor Ca-P	Fair Ca-E
				Poor Ca-E	V. poor Ca-F(?)
				V. poor Ca-F	V. poor Ca-P
			(6·7)	(5·8)	(6·5)
7	—	—	Poor Ca-E	U *	Fair Ca-H
					Fair Ca-E
					V. poor Ca-P
			(6·7)	(10·5)	(6·5)
8	—	—	V. poor Ca-E	—	Fair Ca-H
					Poor Ca-E
					V. poor Ca-P
			(6·7)		(6·5)
9	—	—	V. poor Ca-E	—	Fair Ca-H
					Poor Ca-E
					V. poor Ca-P
			(6·7)		(6·5)

See footnotes to Table 3.

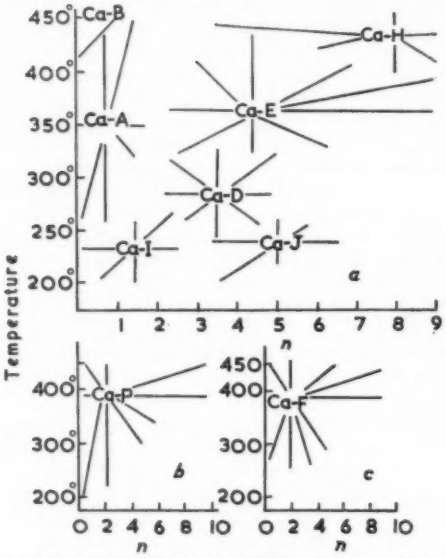
TABLE 6. *Products of crystallisation of gels* $CaO,Al_2O_3,nSiO_2,3NMe_4{\cdot}OH$ + aq.

Reference letter	Identification	Reference letter	Identification
(Ca,N)-A	Boehmite, Al_2O_3,H_2O	(Ca,N)-P	Hexagonal dimorph of anorthite
(Ca,N)-C	Bayerite, $Al_2O_3,3H_2O$	(Ca,N)-V	Montmorillonite-type phase
(Ca,N)-T	Sodalite-type phase	(Ca,N)-G	Gmelinite-type phase
(Ca,N)-L	Cubic harmotome		

(*c*) When mixtures of oxide composition $CaO,Al_2O_3,nSiO_2$ ($1 < n < 9$) were made with silica glass powder in place of the silica sol, better yields of crystals were obtained. Ca-harmotome (Ca-L) appeared over much of the lower temperature field, but Ca-analcite was still an important phase. Species Ca-N, or hydrogrossulars Ca-K poor in silica and therefore near the non-siliceous end member Ca-N, appeared below 210° instead of aluminosilicates. This indicates that the silica glass is unreactive at these low temperatures, so that the system behaves as though the silica component was not present. At about 300° harmotome (Ca-L) crystallised first, and then recrystallised to analcite (Ca-E) after a time greater than 12 days. The products and conditions of crystallisation are shown in Table 5, and crystallisation fields are given in Fig. 3*a*—*c*.

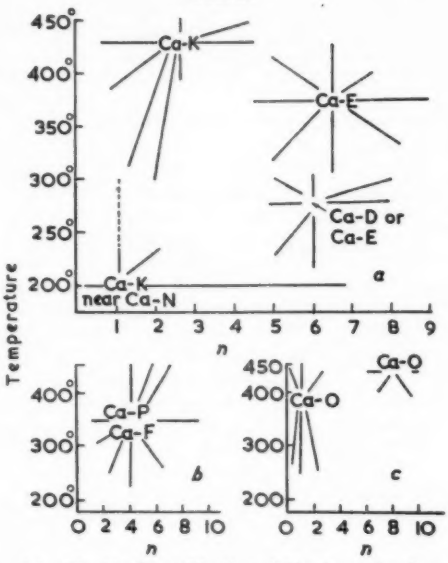
Crystallisation of Calcium Aluminosilicate Gels in Presence of Tetramethylammonium Hydroxide.—Because of the low pH often found in the cold mother-liquors after reaction (Tables

FIG. 1.



(a), (b), (c) Crystallisation fields of some species grown hydrothermally from the four-component system $CaO–Al_2O_3–SiO_2–H_2O$. *The parent gels were of oxide composition* $CaO,Al_2O_3,nSiO_2$ + aq. *The value of n is the abscissa in the Figure.*

FIG. 2.



(a), (b), (c) Crystallisation fields from the four-component system $CaO–Al_2O_3–SiO_2–H_2O$. *The parent gels were of oxide composition* $3CaO,Al_2O_3,nSiO_2$ + aq. *The value of n is the abscissa in the Figure.*

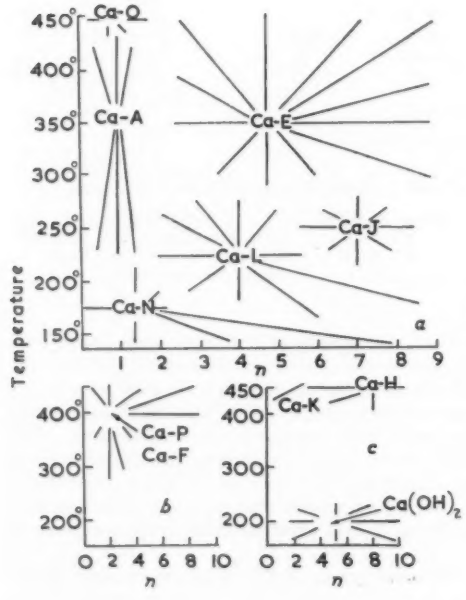


FIG. 3.

(a), (b), (c) Crystallisation fields from the four-component system $CaO–Al_2O_3–SiO_2–H_2O$. *The reaction mixtures were lime + aluminium hydroxide in the molar ratio* 1 : 1 *together with n molar parts of powdered silica* + aq. *The value of n is the abscissa in the Figure.*

3—5), tetramethylammonium hydroxide was added to maintain the pH and so to act as a possible mineraliser. Gels of composition $CaO,Al_2O_3,nSiO_2,\frac{1}{2}NMe_4{\cdot}OH$ + aq. (n = 2 or 4) were first studied. However, little or no crystallisation occurred at 200° in times up to 16 days. Gels of composition $CaO,Al_2O_3,nSiO_2,3NMe_4{\cdot}OH$ + aq. were then found to crystallise within 7 days at 100°, and so were examined further. The organic base became in part a constituent of some of the crystals so that its function was not just that of a mineralising catalyst. The tetramethylammonium ion tended to be hydrolysed under the conditions employed,[17] so that the actual organic ions incorporated are not known. However, all are derived from amine bases, and are given the symbol N. The species formed are summarised in Table 6. The extent to which nitrogenous ions are incorporated must vary from phase to phase. No ions are present in the hydrated aluminas, but nitrogenous sodalites, harmotomes, and montmorillonite-type phases have been synthesised in entire absence of metallic inorganic ions,[17] so that the organic ions can compete with Ca^{2+} for lattice sites. In (Ca,N)-P there may, however, be little nitrogenous material, because the lattice is less open [18] and so less able to provide sites for the larger alkylammonium ions. The bayerite, sodalite, and montmorillonite of Table 6 did not appear in absence of the organic base (cf. Table 1).

Table 7 records the experimental conditions under which the phases of Table 6 appeared. Two methods of making the reaction mixtures were used. In method (*a*) quicklime and alumina gel were ground together, silica sol was added with stirring, and finally the tetramethylammonium hydroxide was also added. In method (*b*) the organic base was first mixed with

TABLE 7. *Crystallisation of mixtures* $CaO,Al_2O_3,nSiO_2,3NMe_4{\cdot}OH$ + aq.*

	Method of mixing and conditions			
	Method (*a*)		Method (*b*)	
n	4 days 150°	7 days 200°	3 days (n = 1—4) 200°	2 days (n = 5—8) 250°
1	Fair (Ca,N)-C Poor (Ca,N)-T	Good (Ca,N)-A	Fair (Ca,N)-A	Fair (Ca,N)-A Fair (Ca,N)-P
2	Poor (Ca,N)-C Fair (Ca,N)-T	Good (Ca,N)-P Poor (Ca,N)-A	Good (Ca,N)-G Poor (Ca,N)-T	Fair (Ca,N)-P
3	Poor (Ca,N)-C Fair (Ca,N)-T	Fair (Ca,N)-P Good (Ca,N)-G Fair (Ca,N)-T	Good (Ca,N)-T Poor (Ca,N)-G	Poor (Ca,N)-L Poor (Ca,N)-T V. poor (Ca,N)-P
4	Poor (Ca,N)-C Fair (Ca,N)-T	Fair (Ca,N)-G Fair (Ca,N)-T	Fair (Ca,N)-T V. poor (Ca,N)-G	Fair (Ca,N)-T Poor (Ca,N)-L
5	Poor (Ca,N)-C	Fair (Ca,N)-G Fair (Ca,N)-T	Poor (Ca,N)-T	Fair (Ca,N)-L Poor (Ca,N)-T
6	Poor (Ca,N)-C	U	U	Poor (Ca,N)-V
7	Poor (Ca,N)-C	U	U	Poor (Ca,N)-V
8 and 9	Poor (Ca,N)-C	U	U	Poor (Ca,N)-L Fair (Ca,N)-T

* U denotes non-crystalline. In every crystallisation, in addition to compounds listed, a very weak X-ray pattern of crystalline $Ca(OH)_2$ was recorded.

alumina gel, the silica sol next stirred in, and finally the solid calcium oxide added. Use of method (*b*) resulted, *inter alia*, in the appearance of the montmorillonite-type phase (Ca,N)-V.

The *d*-spacings of (Ca,N)-G, are recorded in Table 11. This crystal has pronounced similarities to gmelinite and also to chabazite, though there are some differences.[12] The properties of the individual species in Table 7 are not, however, further described since their counterparts produced from nitrogenous aluminosilicate gels free from Ca-ions are discussed elsewhere [17] [with the exception of (Ca,N)-G].

Some Characteristic Synthetic Ca-*aluminates and Aluminosilicates.*—The synthetic boehmite (Al_2O_3,H_2O), corundum (Al_2O_3), bayerite ($Al_2O_3,3H_2O$), and cristobalite (SiO_2) will not be further characterised in this section. Various compounds are, however, considered below.

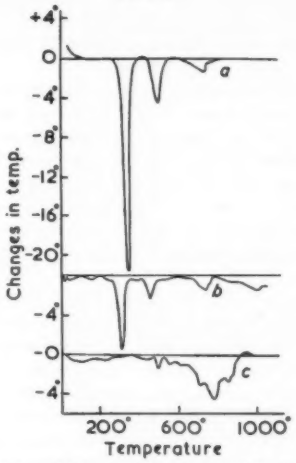
Species Ca-M ($4CaO,3Al_2O_3,3H_2O$). This species was not obtained free of gel, as indicated by the thermogram in Fig. 4, curve *c*. The small endothermic peaks between 20° and 500° appear as a result of the presence of alumina gel mixed with $Ca(OH)_2$. The peak at 705° is also considered to be due to gel. The main peaks at 767° and 850° are attributed to Ca-M,

[17] Barrer and Denny, preceding paper.
[18] Takeuchi and Donnay, *Compt. rend.*, 1959, **248**, 265.

TABLE 8. *Some* d*-spacings (in* Å*) of aluminates and of* Ca-N *and* Ca-K*, and of a natural grossularite garnet.*

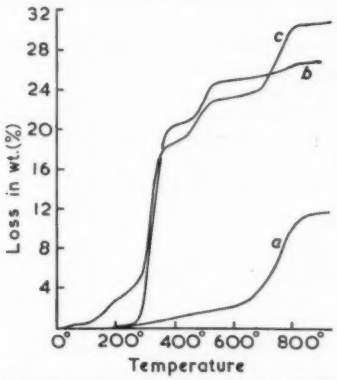
Ca-N			$(3CaO,Al_2O_3,6H_2O)$ [9]		Ca-K		Ca-K		Ca-K		Ca-K		Grossularite [9] garnet		Ca-M $(4CaO,3Al_2O_3,3H_2O)$		$12CaO,7Al_2O_3$ (A.S.T.M. index)		Ignited Ca-N	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
$5{\cdot}11$	vs	211	$5{\cdot}16$	vs	$5{\cdot}16$	m	$5{\cdot}09$	m	—	—	—	—	—	—	$5{\cdot}06$	vw	$4{\cdot}85$	100	$4{\cdot}91$	s
$4{\cdot}42$	m	220	$4{\cdot}47$	m	$4{\cdot}44$	mw	$4{\cdot}39$	w	—	—	—	—	$4{\cdot}14$	vw	$4{\cdot}84$	w	—	—	$3{\cdot}95$	vw
$3{\cdot}35$	ms	321	$3{\cdot}37$	m	$3{\cdot}37$	s	$3{\cdot}30$	w	—	—	—	—	—	—	$3{\cdot}71_5$	w	$3{\cdot}77$	20	$3{\cdot}68$	vw
$3{\cdot}13_1$	m	400	$3{\cdot}15$	m	$3{\cdot}14_9$	s	$3{\cdot}10_5$	w	$2{\cdot}99_9$	w	$2{\cdot}98$	s	$2{\cdot}98$	s	$3{\cdot}57$	vs	$3{\cdot}20$	20	$3{\cdot}2$	w
$2{\cdot}80_9$	vs	420	$2{\cdot}81$	m	$2{\cdot}81_7$	vs	$2{\cdot}78_5$	m	$2{\cdot}68_1$	s	$2{\cdot}66_2$	vs	$2{\cdot}65$	vs	$3{\cdot}45_2$	m	$2{\cdot}98$	50	$3{\cdot}04$	w
$2{\cdot}66_9$	vw	332	—	—	—	—	—	—	—	—	$2{\cdot}52_9$	vw	$2{\cdot}51$	w	$3{\cdot}32_2$	w	$2{\cdot}67$	100	$2{\cdot}68$	vs
$2{\cdot}55_5$	w	422	$2{\cdot}56$	vw	$2{\cdot}56_9$	vw	—	—	$2{\cdot}44_8$	vw	$2{\cdot}42_8$	w	$2{\cdot}42$	m	$3{\cdot}24_6$	s	$2{\cdot}43$	50	$2{\cdot}44$	w
$2{\cdot}45_8$	mw	431	$2{\cdot}46$	w	$2{\cdot}46_9$	w	—	—	$2{\cdot}35_3$	w	$2{\cdot}33_6$	w	$2{\cdot}33$	m	$3{\cdot}07_8$	m	$2{\cdot}18$	50	$2{\cdot}18$	m
$2{\cdot}28_8$	vs	521	$2{\cdot}30$	vs	$2{\cdot}30_2$	s	$2{\cdot}27_7$	w	$2{\cdot}19_0$	vw	—	—	$2{\cdot}16_5$	m	$3{\cdot}00_8$	vs	$1{\cdot}93$	40	—	—
—	—	440	$2{\cdot}22_0$	vw	—	—	—	—	—	—	—	—	$2{\cdot}09_3$	vw	$2{\cdot}84_4$	s	$1{\cdot}66$	40	$1{\cdot}69$	m
$2{\cdot}03_3$	vs	611	$2{\cdot}03_9$	s	$2{\cdot}04_2$	s	$2{\cdot}02_1$	w	$1{\cdot}94_7$	mw	$1{\cdot}93_1$	mw	$1{\cdot}92_8$	s	$2{\cdot}78_0$	m	$1{\cdot}59$	40	$1{\cdot}60$	m
$1{\cdot}98_1$	vw	620	$1{\cdot}99_2$	vw	—	—	—	—	—	—	—	—	$1{\cdot}87_1$	vw	$2{\cdot}60_8$	s				
$1{\cdot}80_8$	w	444	$1{\cdot}81_2$	vw	—	—	—	—	$1{\cdot}73_3$	vvw	$1{\cdot}71_6$	w	$1{\cdot}71_1$	m	$2{\cdot}53_4$	vs				
$1{\cdot}73_7$	m	640	$1{\cdot}74_1$	w	$1{\cdot}74_7$	m	$1{\cdot}72_2$	w	$1{\cdot}66_3$	w	$1{\cdot}64_7$	w	$1{\cdot}64_5$	s	$2{\cdot}40_0$	vw				
$1{\cdot}70_5$	m	633	$1{\cdot}71_1$	w	$1{\cdot}71_4$	w	—	—	—	—	—	—	—	—	$2{\cdot}38_9$	vw				
$1{\cdot}67_5$	ms	642	$1{\cdot}68_0$	m	$1{\cdot}68_2$	m	$1{\cdot}65_1$	w	$1{\cdot}60_2$	mw	$1{\cdot}58_8$	mw	$1{\cdot}53_8$	vs	$2{\cdot}28_9$	s				
$1{\cdot}59_1$	mw	651	$1{\cdot}60_0$	vw	—	—	—	—	—	—	—	—	—	—	$2{\cdot}21_6$	s				
$1{\cdot}56_6$	mw	800	$1{\cdot}57_1$	w	—	—	—	—	—	—	$1{\cdot}48_4$	vw	$1{\cdot}48_6$	m	$2{\cdot}15_4$	m				
$1{\cdot}47_7$	vw	822	—	—	—	—	—	—	—	—	—	—	—	—	$2{\cdot}08_0$	vvs				
$1{\cdot}40_1$	w	840	$1{\cdot}40_5$	w	—	—	—	—	—	—	—	—	—	—	$1{\cdot}91_6$	s				
		752	—	—	—	—	—	—	$1{\cdot}33_6$	vvw	—	—	$1{\cdot}33_7$	m	$1{\cdot}79_2$	m				
		833	—	—	—	—	—	—	$1{\cdot}30_9$	vvw	$1{\cdot}29_8$	vw	$1{\cdot}29_6$	s	$1{\cdot}73_9$	m				
															$1{\cdot}67_9$	w				
															$1{\cdot}59_5$	vs				
															$1{\cdot}56_7$	s				
															$1{\cdot}54_7$	s				
															$1{\cdot}50_8$	m				
															$1{\cdot}40_2$	m				
															$1{\cdot}37_1$	s				
															$1{\cdot}32_0$	m				
$a = 12{\cdot}53$ Å			$a = 12{\cdot}56$ Å		$a = 12{\cdot}60$ Å		$a = 12{\cdot}41$ Å		$a = 12{\cdot}00$ Å		$a = 11{\cdot}89$ Å		$a = 11{\cdot}84$ Å							

FIG. 4.



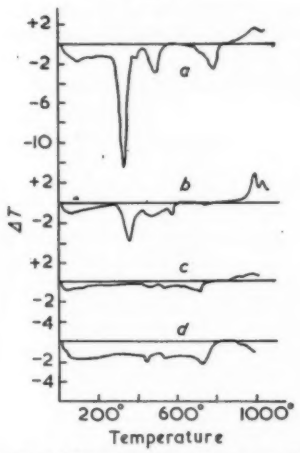
(*a*) *and* (*b*): *Thermograms of* Ca-N ($3CaO,Al_2O_3,6H_2O$) *prepared* (*a*) *at* 125° *for* 26 *days and* (*b*) *at* 200° *for* 9 *days.* (*c*) *Thermogram of* Ca-M ($4CaO,3Al_2O_3,3H_2O$).

FIG. 5.



(*a*) *Thermogravimetric curve of* Ca-M. (*b*) *and* (*c*) *Thermogravimetric curves of two* Ca-N *samples of differing purity.*

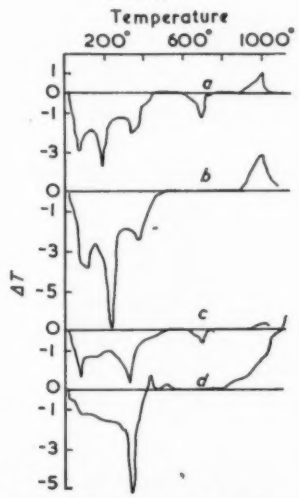
FIG. 6.



(*a*), (*b*), (*c*) *Thermograms of some synthetic hydrogarnets, of differing* Al_2O_3 : SiO_2 *ratios. Samples* (*a*) *and* (*b*) *are very poor in silica and approach* Ca-N *in composition. Sample* (*c*) *is rich in silica* (*Table* 9). *Curve* (*d*) *gives the thermogram of a natural hydrogarnet.*

a: $3CaO,Al_2O_3,SiO_2$ *at* 200° *for* 20 *days.*
b: $3CaO,Al_2O_3,SiO_2$ *at* 220° *for* 19 *days.*
c: $3CaO,Al_2O_3,3SiO_2$ *at* 450° *for* 4 *days.*

FIG. 7.



(*a*) *and* (*b*) *Thermograms of synthetic and naturally occurring* Ca-*thomsonite respectively.* (*c*) *and* (*d*) *Thermograms of synthetic and naturally occurring* Ca-*epistilbite respectively.*

a: $CaO,Al_2O_3,3SiO_2$ (*glass*) *at* 250° *for* 31 *days.*
b: $CaO,Al_2O_3,6SiO_2$ (*glass*) *at* 250° *for* 31 *days.*

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although a thermogram previously given for this compound [3] shows only one smooth endothermic peak at about 730°. The thermogravimetric curve is shown in Fig. 5*a*, and the characteristic *d*-spacings are summarised in Table 8. The 12% loss in weight in the thermogravimetric curve further suggests the presence of gel, since the water content of pure Ca-M is only 9%.

Species Ca-N ($3CaO,Al_2O_3,6H_2O$). This compound is the non-siliceous end-member of the hydrogrossular series designated as Ca-K. As for Ca-M, this phase was not obtained free from gel, the best yield being from the mixture $3CaO,Al_2O_3$ + aq. heated at 125° for 26 days. Thermogravimetric curves of two samples of Ca-N are shown in Fig. 5*b*, *c*. The purer sample (curve *b*) shows negligible water loss up to the first sharp dehydration step starting at about 250° and so indicates absence of gel. 25% of water is lost in the first two steps and since the pure phase Ca-N contains 28·6% by weight of water, the purity of the sample examined may be ~87%. The second sample of Ca-N (curve *c*) is considerably less pure and contains hydrous gel.

The thermograms and differential thermogravimetric curves of Ca-N (Fig. 4*a*, *b*) show good correspondence of peaks indicating that the processes observed in the thermograms are associated with water loss. The main endothermic peaks are at 340° and 500° and the water is lost in steps. The differential thermal analyser was then calibrated by using salt hydrates ($BaCl_2,2H_2O$ and $CuSO_4,5H_2O$) [19] which have known heats of hydration, and was then used to obtain approximate heats of reaction for the purer sample. In the main dehydration step, corresponding to the loss of nearly 5 mol. of water per formula weight, the heat absorbed was ~20·1 kcal. per mole of water lost, and in the second step this heat was ~22·6 kcal. for the loss of the sixth molecule. One of the products of water loss was the phase $12CaO,7Al_2O_3$.[20]

The *d*-spacings of Ca-N are given in Table 8. The cubic unit-cell dimension was 12·56 Å, and the refractive index determined in sodium light was 1·608 ± 0·002.

Species Ca-K (*grossular hydrogarnets of variable* $Al_2O_3 : SiO_2$ *ratios*). A series of solid solutions is believed to exist [9] between the cubic iso-structural compounds $3CaO,Al_2O_3,6H_2O$ (Ca-N) and $3CaO,Al_2O_3,3SiO_2$, for which series the unit cells and *d*-spacings vary continuously with composition from the hydrous aluminate to the anhydrous aluminosilicate (grossular). The temperatures of crystallisation and unit-cell sizes of some hydrogarnets prepared in this work are given in Table 9. From the relation between unit-cell dimensions and composition given

TABLE 9. *Preparation of hydrogarnets from gels* $3CaO,Al_2O_3,nSiO_2$ + aq.

Temp.	*n*	Unit cell edge (Å)	Composn. of product (mol. per $3CaO,Al_2O_3$) SiO_2	H_2O	Temp.	*n*	Unit cell edge (Å)	Composn. of product (mol. per $3CaO,Al_2O_3$) SiO_2	H_2O
200°	1	12·60	0(?)	6·0	350°	3	11·91	2·71	0·58
200	2	12·61	0(?)	6·0	380	1	11·95	2·55	0·90
200	3	12·61	0(?)	6·0	380	2	11·92	2·68	0·64
200	4	12·57	0·05	5·90	380	3	11·92	2·68	0·64
220	1	12·52	0·18	5·64	415	1	11·96	2·51	0·98
220	2	12·50	0·23	5·54	415	2	11·95	2·55	0·90
237	2	12·49	0·27	5·46	415	3	11·92	2·68	0·64
237	2,1	12·06	2·07	1·86	450	2	11·94	2·60	0·80
265	1	12·11	1·81	2·38	450	3	11·97	2·47	1·06
265	2 *	12·41	0·51	4·98	455	2	11·94	2·60	0·80
300	2	12·00	2·35	1·30	450	3	11·89	2·79	0·42
350	2	11·90	2·75	0·50					

* SiO_2 glass as source.

by Flint, McMurdie, and Wells [9] the compositions of the hydrogarnets of Table 9 have been estimated. These compositions fall into a high- and a low-silica field. The high field has composition limits $1·81 < SiO_2 < 2·79$ per residue $3CaO,Al_2O_3$, the low field has limits $0 < SiO_2 < 0·51$, and it is therefore possible that an immiscibility gap exists. The less hydrated crystals were obtained at higher temperatures. Species Ca-K was not prepared in a pure state, and was commonly admixed with Ca-P, Ca-F (anorthite), or Ca-O. The thermograms of several hydrogarnets are shown in Fig. 6*a*—*c*, curve *d* referring to a natural hydrogrossular. They should be compared with the thermograms of Fig. 4 for Ca-N.

[19] Barrer and Langley, *J.*, 1958, 3817.
[20] A.S.T.M. index.

TABLE 10. *Some* d*-spacings of synthetic* Ca*-zeolites and of their natural counterparts.*

Harmotome					Thomsonite					Epistilbite					Ca-Analcites						
Tetragonal Ca-harmotome [21]			Ca-L		Natural (A.S.T.M. index)			Ca-I		Natural			Ca-J		Wairakite [a]			Ca-E		Ca-D	
hkl	*d*	*I*	*d*	*I*	*hkl* [b]	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*
110	7·1	s	7·14	vs	022	4·63	67	4·63	m	020	8·85	m	8·89	s	200	6·85	m	6·80	m	6·82	m
002	4·94	s	4·96	ms	312	—	—	3·50	m	210	6·85	m	6·88	s	211	5·57	vs	5·54	vs	5·56	vs
211	4·12	s	4·14	s	132	3·45	53	—	—	—	—	—	[5·54	mw]	220	4·84	m	4·80	m	4·82	m
112	4·05	ms	4·07	w	322,232	3·18	40	$3·19_7$	w	002	4·89	s	4·89	s	321	3·64	m	3·63	w	3·63	m
311	3·22	m	$3·24_0$	m	204,024	2·93	100	$2·94_2$	m	230,102	4·63	vw	—	—	400	3·42	s	$3·40_3$	vs	$3·40_3$	vs
103	3·12	s	$3·14_2$	vs	412,142	2·84	13	$2·85_8$	m	040	4·47	vw	4·48	w	004	3·39	vs	—	—	$3·37_1$	s
222	2·87	m	—	—	242,422	2·66	43	$2·67_2$	m	022	4·32	m	4·31	mw	332	$2·90_9$	s	$2·90_3$	vs	$2·90_7$	s
213	2·66	s	$2·67_4$	ms		2·24	27	$2·25_0$	w	240,212	3·98	vw	—	—	323	$2·89_7$	m	—	—	$2·89_3$	m
400	2·55	mw	$2·56_6$	vw		2·17	33	$2·17_9$	w	141	3·90	vw	—	—	431	$2·68_0$	m	$2·67_0$	m	$2·66_9$	w
303	2·33	m	$2·33_2$	vw		1·81	36	—	—	240,330	3·84	s	3·87	s	—	2·67	vw	—	—	—	—
204	2·20	w	—	—		1·74	23	$1·76_9$	vw	032	3·78	w	—	—	125	$2·48_9$	m	$2·48_6$	m	$2·47_9$	w
323	2·12	w	$2·12_8$	vw		1·61	8	$1·62_6$	vw	400,222	3·71	w	—	—	440	$2·41_8$	w	$2·40_9$	w	$2·40_7$	w
422	2·06	mw	$2·07_1$	vw		1·46	36	—	—	312	3·42	vs	$3·44_4$	vs	116	$2·21_3$	m	$2·21_2$	w	$2·20_4$	vw
224	2·02	w	—	—						042	3·31	vw	$3·33_4$	w	640	$1·89_5$—	m (diff)	$1·88_9$	w	$1·88_9$	vw
005	$1·97_5$	mw	$1·98_7$	vw							3·24	w	$3·25_1$	w		$1·88_6$					
314	$1·93_0$	mw	$1·94_4$	vw							3·19	ms	$3·20_5$	ms	633	$1·85_7$	w	$1·85_5$	w	$1·85_3$	vw
215	$1·80_5$	mw	$1·81_6$	vw							3·03	vw	—	—	327	$1·73_2$—	m (diff)	—	—	$1·72_5$	vw
440	$1·77_0$	mw	$1·78_3$	mw							2·90	m	$2·91_5$	mw		$1·72_2$					
522	$1·73_5$	mw	$1·74_3$	vw							2·84	m	$2·85_3$	m	741	$1·68_0$	w (diff)	$1·68_9$	w		
433	$1·70_5$	mw	$1·71_6$	w							2·76	vw	$2·78_7$	w	(811,554)						
600	$1·66_5$	w	$1·67_5$	vw							2·68	w	$2·68_4$	m	831,743	$1·58_6$	w	$1·58_4$	w		
610	$1·64_0$	mw	$1·65_0$	vw							2·66	w	—	—	(750)						
116	$1·60_2$	w	—	—							2·54	w	$2·50_9$	m							
800	—	—	$1·26_1$	w									$2·41_7$	w							
													$2·21_1$	vw							
													$2·09_3$	vw							
													$1·86_6$	vw							
													$1·77_6$	w							
$a = 10·01$ Å			$a = 10·01$ Å							$a = 14·9$ Å [c]			$a = 15·0$ Å [c,d]		$a = 13·68$ Å			$a = 13·62$ Å		$a = 13·62$ Å	
$c = 9·87$ Å			$c = 9·89$ Å							$b = 17·87$ Å			$b = 17·0$ Å		$b = 13·56$ Å			$c = 13·56$ Å			
										$c = 10·32$ Å			$c = 10·25$ Å								
										$\beta = 90° 40'$			$\beta = \sim 90°$								

[a] Steiner, *Min. Mag.*, 1955, **30**, 691; Coombs, *ibid.*, p. 699. [b] Indexing on the basis of a unit cell $a = 13·0$, $b = 13·1$, $c = 13·2$ Å. [c] Near orthorhombic pseudo-cells; a somewhat smaller monoclinic unit cell can also be given (Strunz and Tennyson, *Neues Jahrb. Min.*, 1956, **1**, 1). [d] Obtained from the electron-diffraction pattern of another sample.

TABLE 11. *Some* d*-spacings of synthetic* Ca*-aluminosilicates.*

Anorthite (A.S.T.M. index)		Ca-F		Ignited Ca-harmotome		Ignited Ca-analcite		Ca-P Davis and Tuttle [6]			Ca-P This work		Ca-O		(Ca,N)-G	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
6·39	40	—	—	6·40	w	—	—	002	7·37	85	7·33	vw	3·59	s	11·6	vw
—	—	[5·55]	vs	[5·4]	w	—	—	100,010	4·43	7	4·42	s	$3·11_5$	vw	9·21	vs
4·61	40	[4·80]	w	—	—	—	—	102,012	3·80	30	3·79	vs	$3·02_7$	m	7·62	m
4·04	60	4·07	vw	4·10	w	4·09	vw	004	3·68	100	3·67	s	$2·78_7$	vs	6·67	mw
—	—	—	—	3·99	m	3·96	mw	104,014	2·84	40	$2·83_2$	vs	$2·54_3$	m	6·32	vs
3·70	40	3·69	s	3·69	m	3·69	m	110	$2·55_5$	9	$2·55_6$	vs	$2·35_3$	m	5·39	mw
3·57	60	—	—	—	—	—	—	006	$2·45_6$	14	—	—	$2·20_2$	w	4·60	m
—	—	3·42	vvs	3·45—3·34	m (diff)	3·48	vw	112	$2·41_4$	3	$2·41_5$	vw	$2·07_5$	m	4·48	s
—	—	—	—	—	—	3·34	w	106,016	$2·14_7$	11	—	—	$1·86_5$	vw	4·20	ms
3·19	100	$3·19_6$	vs	3·18	vs	3·18	vs	202,022	$2·11_9$	4	$2·11_9$	w	$1·79_6$	vw	3·78	vs
2·96	60	$2·93_5$	s	2·87	vw	2·96	m	008	$1·84_2$	100	$1·84_2$	m	$1·74_3$	vw	$3·32_2$	w
2·79	60	$2·84_5$	s	2·82	w	2·83	w	116	$1·77_0$	9	$1·77_0$	w	$1·55_6$	ms	$3·17_0$	m
2·65	40	$2·67_6$	m	2·67	w	—	—	118	$1·49_5$	14	—	—	$1·51_2$	w	$2·95_7$	w
2·51	70	$2·50_4$	m	2·53	w	2·52	vw	1,0,10; 0,1,10	$1·39_9$	12	—	—	$1·43_0$	vw	$2·87_2$	mw
—	—	—	—	2·50	w	—	—								$2·70_0$	mw
2·38	20	—	—	2·41	w (diff)	—	—	2,0,10; 0,2,10	$1·27_7$	9	—	—			$2·50_6$	m (diff)
2·24	20	$2·21_0$	w	2·20	w	2·17	vw								$2·39_2$	vw
2·13	50	$2·11_6$	s	2·14	w	2·13	vw								$2·34_4$	vw
2·08	40	$2·08_4$	w	2·07	w	—	—								$2·21_7$	vw
2·02	40 (diff)	$2·00_2$	vw	—	—	—	—								$2·00_1$	vw
1·94	40 (diff)	$1·88_6$	m	1·90	vw	—	—								$1·79_0$	m
1·84	20	$1·84_0$	s	1·83	w (diff)	1·82	vvw								$1·66_6$	mw
1·79	50	$1·78_9$	s	—	—	—	—								$1·59_6$	vvw
1·76	60	$1·74_7$	m	$1·76_1$	m	1·76	vvw								$1·41_7$	vw
1·71	40	—	—	—	—	1·71	vvw								$1·29_0$	vw
1·62	40	$1·62_7$	vw	$1·60_9$	vw										$1·21_8$	vw
1·54	20	$1·55_8$	vvw	—	—											
1·48	60	$1·48_5$	m	$1·51_5$	vw											
1·45	20	$1·46_0$	vs	$1·46_3$	vw											
1·41	20	—	—	$1·43_5$	vw											
1·39	50	$1·40_1$	m													
1·36	60	—	—													
1·34	60	$1·34_3$	m													
1·32	20	—	—													
1·30	20	$1·29_8$	w													
1·27	40	$1·27_3$	s													
1·24	20	$1·25_8$	vw													
1·21	40	$1·21_0$	m													
1·08	20	$1·10_5$	vw													

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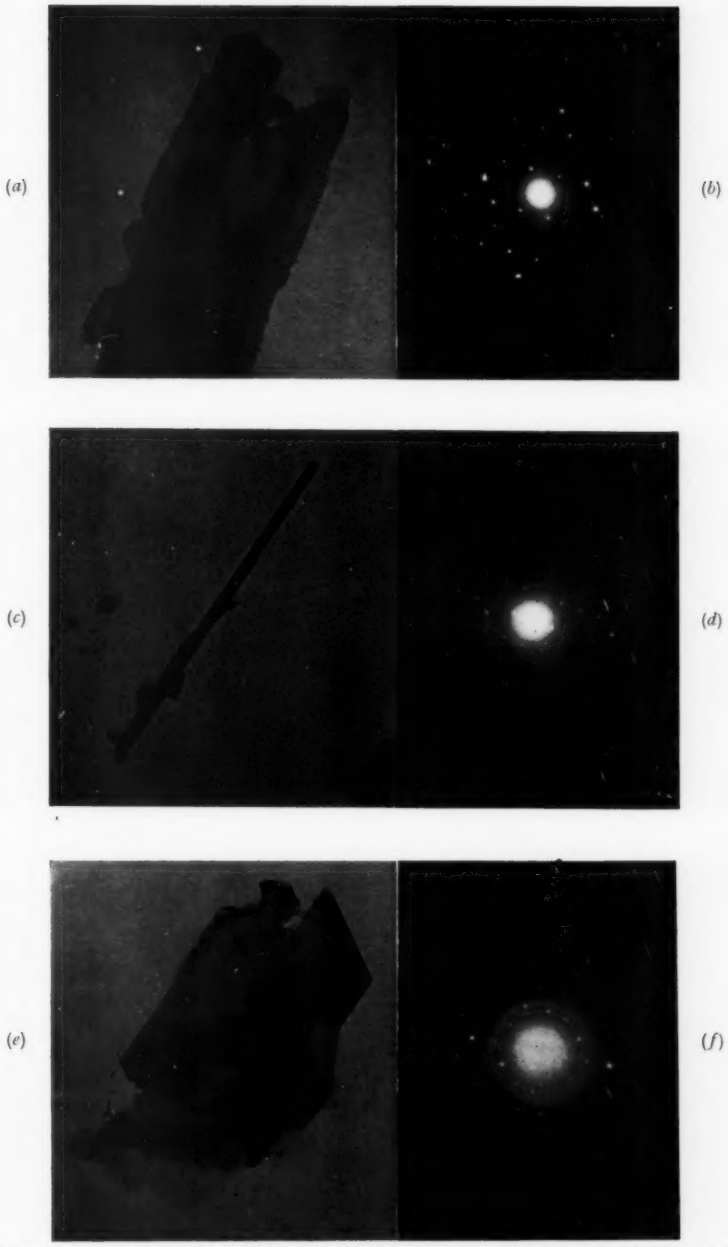

(a), (c), and (e) are electron micrographs of synthetic epistilbite, mordenite, and the hexagonal dimorph of anorthite, respectively; (b), (d), and (f) are the corresponding electron-diffraction patterns.

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Some *d*-spacings of Ca-N, of several samples of Ca-K, and of a natural grossular are compared in Table 8. The refractive index of a hydrogarnet having a unit-cell edge of 11·97 Å was 1·665 ± 0·004.

Zeolites. The zeolites formed belonged to the analcite, harmotome, thomsonite, epistilbite, and mordenite groups. Several of these species are described below.

Species Ca-L (*calcium harmotome*). This zeolite was most readily prepared, in good but not 100% yield, from mixtures $CaO,Al_2O_3,nSiO_2$ when silica glass was the source of silica (Table 5). The thermograms of this mineral and of a Ca-harmotome prepared by ion-exchange from synthetic Na-harmotome [13,21] are shown in Fig. 7*a* and *b* respectively. The peak for Ca-L at about 700° is associated with the presence of gel, but otherwise the similarity is clear. The thermogram and differential thermogravimetric curves corresponded closely so that the endothermic peaks are all associated with water loss. By considering the water loss in the range 20—460° to be from Ca-harmotome only, the heat of dehydration was evaluated, as for Ca-N. It was about 28·4 kcal. per mole of water lost.

The Ca-harmotome sample examined by *X*-ray powder photograph was tetragonal with $a = 10{\cdot}10$ and $c = 9{\cdot}89$ Å. The *d*-spacings are compared in Table 10 with those of the Ca-harmotome prepared by ion exchange.[21] The refractive index of a specimen prepared from a mixture $CaO,Al_2O_3,3SiO_2$ + aq. at 250° was 1·510 ± 0·003.

Species Ca-I (*calcium thomsonite*). Calcium thomsonite (Table 3) was admixed with gel, Ca-P, or boehmite. Although the yield was low the thermogram resembled that of natural thomsonite. The comparison of peak heights suggests about a 20% yield of synthetic thomsonite. The peak at about 745° is due to gel. The *d*-spacings are compared with those of natural thomsonite in Table 10.

Species Ca-J (*calcium epistilbite*). This zeolite was obtained from systems $CaO,Al_2O_3,nSiO_2$ + aq., both sol and powdered glass being used as source of the silica (Tables 3 and 5), although the better yields were obtained from the latter. The thermogram of a sample of synthetic Ca-J is compared with that of a natural epistilbite in Fig. 7*c*, *d*. The peak with its maximum at about 700° is due to a small amount of gel. The thermogravimetric curve, shown in Fig. 8, gives a maximum water loss of 16%. The heat associated with the first 13·2% water loss was evaluated as ~21·3 kcal./mole. The *d*-spacings of Ca-J are given in Table 10. The electron-diffraction pattern and an electron micrograph are shown in Plate *b* and *a*, for a specimen of Ca-epistilbite obtained from a gel $CaO,Al_2O_3,4SiO_2$ + aq. crystallised at 225°. The diffraction pattern corresponds to a monoclinic but nearly orthorhombic unit cell $a = 15{\cdot}0$, $b = 17{\cdot}0$, $c = 10{\cdot}25$ Å, and $\beta \sim 90°$. The *X*-ray powder pattern of a natural epistilbite gave $a = 14{\cdot}9$, $b = 17{\cdot}87$, $c = 10{\cdot}32$ Å, and $\beta = 90°\ 40'$; an alternative monoclinic unit cell with $a = 9{\cdot}1$, $b = 17{\cdot}87$, $c = 10{\cdot}32$ Å, and $\beta = 125°\ 3'$ can also be chosen, analogous to that given by Strunz and Tennyson.[22] The micrograph shows the lamellar habit of the crystals.

Species Ca-Q (*calcium mordenite*). Plate *d*, *c* shows the electron diffraction pattern and micrograph of a crystal of Ca-mordenite from a sample obtained by crystallising a gel $CaO,Al_2O_3,7SiO_2$ + aq. at 390°. The crystals are acicular in habit, and the electron-diffraction pattern gives an orthorhombic unit cell of dimensions $a = 18{\cdot}5$, $b = 20{\cdot}3$, and $c = 7{\cdot}55$ Å. Na-mordenite has been prepared in good yield at lower temperatures,[13,23] and it has also been made under conditions similar to those noted above.[7,8]

Species Ca-D (*tetragonal calcium analcite*). Species Ca-D was a variety of analcite similar to the natural mineral, wairakite.[24] It was common over a wide range of temperature and composition, although admixed with gel, Ca-F or Ca-P. The thermogram shows similarity with that of wairakite (Fig. 9*a*, *b*). The thermogravimetric curve of Ca-D in Fig. 10 refers to a sample containing some gel, so that it appears to contain more water (11·2%) than wairakite (8·35%). The *d*-spacings are compared in Table 10 with those of wairakite and of Ca-E. The tetragonal unit cell had dimensions $a = 13{\cdot}62$, $c = 13{\cdot}56$ Å. The factor $c/a = 0{\cdot}995$ was the same for samples prepared at different temperatures. The refractive index of Ca-D was 1·496.

Species Ca-E (*cubic calcium analcite*). Species Ca-E was best synthesised at 350° from mixtures $CaO,Al_2O_3,4SiO_2$ + aq. with powdered silica glass as the source of silica. Thermogram

[21] Barrer, Bultitude, and Kerr, *J.*, 1959, 1521.
[22] Strunz and Tennyson, *Neues Jahrb. Min.*, 1956, **1**, 1.
[23] Barrer, *J.*, 1948, 2158.
[24] Steiner, *Min. Mag.*, 1955, **30**, 691; Coombs, *ibid.*, p. 699.

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and thermogravimetric curves are shown in Figs. 9 and 10, curves *c*. The thermogram shows distinct differences from those of Ca-D or wairakite. The thermogravimetric water loss is 6·80%, and the yield of Ca-E in the sample is therefore estimated at 80%, since the thermogram showed an absence of gel in the product. The *d*-spacings are given in Table 10; the cubic unit-cell edge was 13·62 Å, and the refractive index of the small, often irregular crystallites was 1·493 ± 0·004.

Additional Aluminosilicates.—Characteristics of several additional Ca-aluminosilicates are given below.

Species Ca-F (*calcium felspar*). Calcium felspar was of common occurrence in all crystallisation fields, above about 250° (Tables 3—5, Figs. 1—3). It was usually mixed with gel or another crystalline phase, often Ca-P. The *d*-spacings of Ca-F are compared in Table 11 with

FIG. 8. *Thermogravimetric curves of* (*a*) *synthetic* Ca-*epistilbite and* (*b*) *synthetic* Ca-*harmotome.*

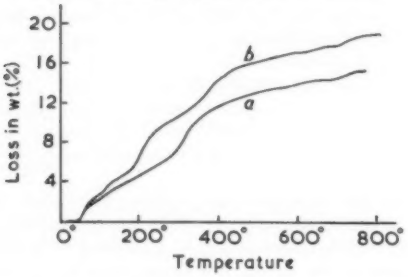


FIG. 10. *Thermogravimetric curves of* (*a*) *tetragonal* Ca-*analcite* (+ *some gel*), (*b*) *natural wairakite, and* (*c*) *cubic synthetic* Ca-*analcite.*

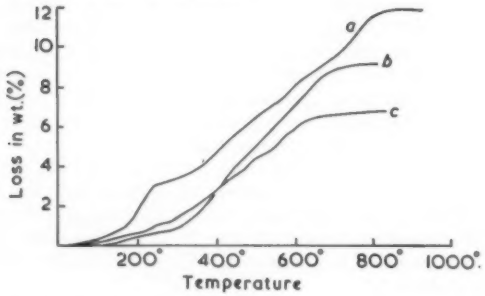
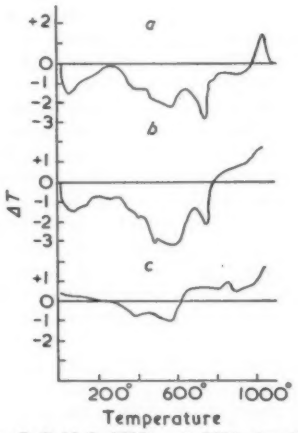


FIG. 9. *Thermograms for* (*a*) *synthetic tetragonal* Ca-*analcite* (*b*) *a natural wairakite, and* (*c*) *synthetic cubic* Ca-*analcite.*



a: $CaO,Al_2O_3,3SiO_2$ *at* 300° *for* 31 *days.*
b: $CaO,Al_2O_3,4SiO_2$ *at* 300° *for* 12 *days.*

those of anorthite, and of some related products prepared by ignition of other species. Some interesting differences arise in these *d*-spacings and their intensities.

Species Ca-P. This phase was a hexagonal dimorph of anorthite,[6] which was also common in all aluminosilicate crystallisation fields, and which first appeared at temperatures as low as 200° (Tables 3—5 and Figs. 1—3). The electron-diffraction pattern and electron micrograph of Plate *f*, *e* clearly show the hexagonal symmetry of this compound. *d*-Spacings are summarised in Table 11, and are compared with those of a preparation by Davis and Tuttle.[6] The latter preparation was stated to be preferentially orientated, the strongest lines all being 00*l*. Orientation may thus account for the differences in observed relative intensities between their preparation and that in Table 11 obtained in our work. Species Ca-P was stable to heating in the differential thermal analysis apparatus up to at least 1050°.

Species Ca-O. The *d*-spacings of this unidentified phase, obtained in major yield, are given in Table 11, to permit its subsequent identification and characterisation.

Discussion

The hydrothermal study reported in this paper has shown that a number of hydrated minerals may be formed under controlled conditions. It has, however, also been possible to prepare anhydrous phases such as corundum, cristobalite, Ca-P, and Ca-F, and it was of interest to find whether other anhydrous materials can be made by sintering the hydrated

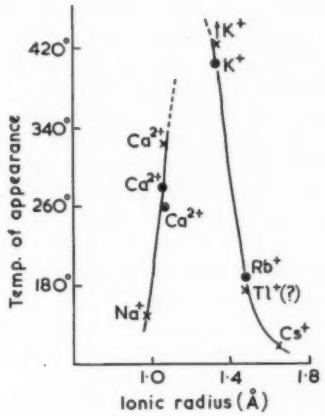


FIG. 11. *Apparent correlation between the lowest temperatures observed for hydrothermal analcite formation from gels, and the radius of the cation present.*
× *Cubic analcites.* ⊗ *Tetragonal analcites.*

species. Table 12 summarises the results of such experiments. From the aluminosilicates only Ca-F or Ca-P are formed, often with amorphous material. The calcium aluminate hydrates can yield an aluminate of composition $12CaO,7Al_2O_3$, and CaO. The *d*-spacings of the phase $12CaO,7Al_2O_3$ are given in Table 8.

The alkali-metal aluminosilicates crystallised most readily when the source of silica

TABLE 12. *Ignition products from hydrated calcium aluminates and aluminosilicates.*

Materials ignited	Temp. ignition	Products
Ca-analcites (cubic and tetragonal) + trace of Ca-P	840°	Amorphous and v. poor Ca-P
	1030	Ca-P + near anorthite
	1080	Ca-P + near anorthite
Natural thomsonite	1030	Near anorthite
Synthetic thomsonite (+ gel + Ca-P)	1030	Near anorthite + Ca-P
Natural epistilbite	1050	Amorphous
Synthetic Ca-epistilbite and gel (from mix using silica sol)	1050	Near anorthite
Synthetic Ca-epistilbite (from mix using powdered silica glass)	1020	Mainly amorphous + v. poor Ca-P + a trace of anorthite (?)
Synthetic Ca-harmotome	850	Mainly amorphous
Synthetic Ca-harmotome (from mix using SiO_2 sol)	1000	Near anorthite
Synthetic Ca-harmotome (from mix using powdered SiO_2 glass)	1020	Near anorthite
Synthetic hydrogrossular ($3CaO,Al_2O_3,2{\cdot}45SiO_2,1{\cdot}1H_2O$)	1000	No change
Natural grossular	1000	No change
Ca-M ($4CaO,3Al_2O_3,3H_2O$) + gel	1030	Unidentified product
Ca-N ($3CaO,Al_2O_3,6H_2O$) + gel	410	$12CaO,7Al_2O_3$ + (?)
	560	$12CaO,7Al_2O_3$ + (?)
	1040	$12CaO,7Al_2O_3$ + CaO + (?)
Non-crystalline product from gel $CaO,Al_2O_3,3SiO_2$ + aq at 225° C.	1030	Near anorthite

in the gel was a sol of high surface area;[12,13] the calcium aluminosilicates, however, have as a rule been shown to behave in the opposite way. Our observation that the crystals formed may depend on the nature and history of the parent gel or mixture is confirmed

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by a similar observation by Ellis.[8] The zeolites produced most readily in the Ca-aluminosilicate crystallisation fields differ on the whole from those most easily formed in crystallisation fields of the alkali-metal aluminosilicates. Analcites, however, are of universal occurrence in all fields, except that of the lithium aluminosilicates.[25] By direct synthesis, analcitic phases of sodium, potassium (two forms), rubidium (two forms), cæsium, thallium, ammonium, and calcium (two forms) have been prepared. A correlation exists between unit-cell dimensions of various forms of the analcitic phases, the diameter of the cation, and whether or not the water is also present in the crystal lattice.[26]

The lowest crystallisation temperatures of analcites appear to vary greatly, and again a correlation is found between these temperatures and the ionic radius, as shown in Fig. 11. The correlation, for lower crystallisation temperatures, is of course likely to be influenced in part by the reactivity of the parent gel or mixture. It is noteworthy that so far the largest ion forming an analcite is Cs^+. Various methylammonium aluminosilicate gels have been crystallised, but analcites were not found in the products.[17] There is probably insufficient room in the analcite-type of aluminosilicate framework to accommodate such large cations. The correlation shown in Fig. 11 is in part related to the basigenic character of the metal, but this is not the only factor, since it appears more difficult to form potassium analcites than it is to make calcium analcites.

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[*Received, June 2nd,* 1960.]

[25] Barrer and White, *J.*, 1951, 1167.
[26] Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.

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203. *Aminodiarylboranes and their Phosphorus and Arsenic Analogues.*

By G. E. Coates and J. G. Livingstone.

Several monomeric aminodiarylboranes ($Ar_2B{\cdot}NR_2$) have been prepared, and their infrared spectra and dipole moments studied. Aminodiphenylborane (R = H) is dimeric and non-polar in benzene solution. The monomeric aminodiarylboranes have low dipole moments, whose direction is reversed on passing from $Ph_2B{\cdot}NMe_2$ to $Ph_2B{\cdot}NPh_2$. Phosphinodiarylboranes are monomeric and not readily hydrolyzed. Their dipole moments are generally greater than those of corresponding amino-compounds, and the phosphino-group is at the negative end of the dipole. The arsino-derivatives are similar but rather less polar. The properties of the phosphorus and arsenic compounds are interpreted in terms of weak π-donor character of phosphorus and arsenic towards boron (in contrast to the strong π-donor character of nitrogen), and the co-ordinative saturation of boron by the aryl groups.

Compounds in which an atom of acceptor character is covalently bound to one of donor character can achieve co-ordination saturation either by the formation of a double bond or by association. The first situation is exemplified by (dimethylamino)dimethylborane, $Me_2B{=}NMe_2$, since the force constant of the B–N bond is appropriate for a double bond.[1] Similarly the force constant of the B–N bonds in trisdimethylaminoborane,[2] $(Me_2N)_3B$, is $5{\cdot}5 \times 10^5$ dyne cm.$^{-1}$ which is appropriate for bonds of order 4/3. Valency expansion by the formation of a fourth σ-bond occurs in the dimeric forms of the chlorides, *e.g.*,

[1] Becher and Goubeau, *Z. anorg. Chem.*, 1952, **268**, 133.
[2] Becher, *Z. anorg. Chem.*, 1956, **287**, 285.

$(Me_2N{\cdot}BCl_2)_2$,[3,4] and in the much studied phosphinoboranes in which cyclic trimers $(Me_2P{\cdot}BMe_2)_3$,[5] tetramers $(Me_2P{\cdot}BH_2)_4$,[5] and polymers [6] are found. No monomeric phosphino- or arsino-boranes appear to have been described, with the possible exception [5] of $PH_2{\cdot}BMe_2$.

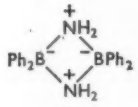
The absence of any general rule which might be used to predict whether a compound of this type would be monomeric (and presumably contain a partial double bond) or associated suggested the need to obtain further data concerning (*a*) circumstances in which aminoboranes are associated, and (*b*) the possible existence of monomeric phosphino- and arsino-boranes.

Aminoboranes.—Unsubstituted aminoborane [7] appears to be polymeric, $(H_2B{\cdot}NH_2)_n$, and unstable. The extent of association decreases as hydrogen is substituted by alkyl groups: thus *N*-methylaminoborane is trimeric,[8] $(H_2B{\cdot}NHMe)_3$, and reversible monomer–dimer equilibria may be realized with $H_2B{\cdot}NMe_2$,[9] $MeHB{\cdot}NMe_2$,[10] $Me_2B{\cdot}NHMe$,[11] and $Me_2B{\cdot}NH_2$.[12] All known tetrasubstituted aminoboranes ($R_2B{\cdot}NR'_2$; R, R′ = alkyl or aryl) appear to be monomeric.[13] Relatively few *B*-arylaminoboranes have been studied, but methylaminodiphenylborane, $Ph_2B{\cdot}NHMe$, slowly changes from monomer to dimer at room temperature; [14] all others described are monomeric.

Aminodiphenylborane has now been prepared from ammonia and chlorodiphenylborane in the presence of triethylamine,

$$Ph_2BCl + NH_3 + NEt_3 = \tfrac{1}{2}(Ph_2B{\cdot}NH_2)_2 + Et_3N,HCl$$

and is dimeric (cryoscopically in benzene and in nitrobenzene). The most likely structure (I) is centrosymmetric, and the observed electric polarization is in agreement with this. The total polarization, measured in benzene solution at 25°, was 119·9 c.c. The electron polarization, measured at six wavelengths and extrapolated to infinite wavelength, was 102·4 c.c., and the difference, 17·5 c.c., is about the expected value of the atom polarization in co-ordination compounds containing balanced dipoles [*e.g.*, the atom polarizations of *trans*-$(R_3P)_2PdAr_2$ complexes are usually about 20 c.c.[15]]. The dipole moment of compound (I) is therefore zero.



(I)

Thus the only dimeric aminodiarylboranes are those containing NH_2 or NHMe groups. Experiments with molecular models indicate that any larger groups attached to the nitrogen would cause substantial steric interference even with the hydrogen atoms in *ortho*-positions on the aryl groups.

All the other aminodiarylboranes prepared in this investigation were monomeric in nitrobenzene solution, though often slightly associated in benzene particularly in the more concentrated solutions. The aminodiarylboranes, $Ar_2B{\cdot}NR_2$, were prepared by three methods:

$$Ar_2BCl + LiNR_2 = Ar_2B{\cdot}NR_2 + LiCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Ar_2BCl + R_2NH + Et_3N = Ar_2B{\cdot}NR_2 + Et_3NHCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$2ArMgBr + Cl_2B{\cdot}NR_2 = Ar_2B{\cdot}NR_2 + MgCl_2 + MgBr_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Method (3) was particularly suitable for the preparation of dimethylaminoboranes.[13]

[3] Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 77.
[4] C. A. Brown and Osthoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2340.
[5] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.
[6] Wagner and Caserio, *J. Inorg. Nuclear Chem.*, 1959, **11**, 259.
[7] Schaeffer, Adams, and Koenig, *J. Amer. Chem. Soc.*, 1956, **78**, 725.
[8] Bissot and Parry, *J. Amer. Chem. Soc.*, 1955, **77**, 3481.
[9] Wiberg, Bolz, and Buchheit, *Z. anorg. Chem.*, 1948, **256**, 285.
[10] Burg and Boone, *J. Amer. Chem. Soc.*, 1956, **78**, 1521.
[11] Wiberg and Hertwig, *Z. anorg. Chem.*, 1947, **255**, 141.
[12] Wiberg and Buchheit, F.I.A.T. Review of German Science, 1948, Inorganic Chemistry, Vol. I, p. 218.
[13] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 5553.
[14] Mikhailov and Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1482.
[15] Coates and Dixon, unpublished observations.

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The ultraviolet spectrum of (diphenylamino)diphenylborane is similar in general appearance to that of tetraphenylethylene [16] (both measured in cyclohexane), absorption maxima and extinction coefficients being at 282 mμ (18,200) and 312 mμ (14,000) respectively.

The infrared spectra of these two compounds are nearly identical, the main differences being the splitting of the C_{ar}–H out-of-plane deformation bands (already reported,[17] and observed by us in all our diarylboron compounds) and the very strong band at 1372 cm.$^{-1}$ in the region in which B–N absorptions are commonly found.[13] The band due to B–N

TABLE 1. *Aminodiarylboranes.*

Aminodiarylborane	B–N absorption frequency (cm.$^{-1}$)	Dipole moment (D)	Degree of association: Benzene Wt. %	Benzene *n*	Nitrobenzene Wt. %	Nitrobenzene *n*
$Ph_2B{\cdot}NH_2$	1552 [b]	0	0·38	1·94	1·90	1·97
	(NH ν, 3320 and 3362) [b]		0·43	1·97	3·37	1·87
			0·68	2·19	4·44	1·94
					5·27	1·93
$Ph_2B{\cdot}NMe_2$	1388 [b]	1·6	3·49	1·08	3·06	0·85
			4·43	1·24	4·41	0·95
			7·59	1·27	5·76	1·06
			9·95	1·17	7·52	1·14
$(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}NMe_2$ ...	1410 [b]	1·1	0·63	0·93	2·07	0·98
			1·09	1·02	3·56	0·92
			1·42	1·16	4·66	1·02
			1·71	1·21	5·53	1·06
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}NMe_2$ ...	1356 [b]	3·1	0·346	0·96	0·209	1·01
			0·588	0·91	0·479	1·09
			0·894	0·95	0·641	1·11
			1·034	0·99	0·743	1·14
$Ph_2B{\cdot}NPh_2$	1372 [a]	1·0	0·774	1·03	0·911	0·97
			1·152	1·31	1·431	0·94
			1·924	1·48	1·827	0·94
			2·259	1·74	2·249	1·10
$Ph_2B{\cdot}N(C_6H_4Me\text{-}p)_2$ ...	1361 [a]	0·8			0·417	1·04
					1·228	1·09
					1·905	1·14
					2·536	1·25
$(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}NPh_2$ ...	1385 [a]	1·6	0·424	1·02	0·579	0·99
			0·763	1·05	1·162	1·04
			1·297	1·14	1·647	1·05
			1·384	1·17	2·06	1·10

[a] In KI disc. [b] In benzene solution.

absorption was always strong and easily recognized in aminoboranes, and its frequency in the various compounds examined is given in Table 1, which also summarizes dipole moments and degrees of association in benzene and in nitrobenzene. The aminoboranes listed in Table 1 are all readily hydrolyzed by cold water; this is a general property of aminoboranes and was the basis of a method sometimes used for their analysis.

The B–N frequencies of all but the first compound in Table 1 fall within the range 1330—1530 reported [13] for eleven other aminoboranes. A variation in these frequencies has generally been interpreted as mainly due to a change in the multiplicity of the B–N bond,[1,2,13] so the high frequency (1552) observed * in the case of the dimeric compound (I), in which the B–N bonds must surely be single, may at first sight appear remarkably high. However, vibrational modes due to the stretching of B–N bonds in a ring can scarcely be expected to be closely comparable to those due to an isolated B–N bond in a monomeric compound.

* This frequency was also observed when the substance was pressed in a potassium iodide disc.

[16] Kortüm and Dreesen, *Chem. Ber.*, 1951, **84**, 182.
[17] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

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Although the tetramethyl compound $Me_2B{\cdot}NMe_2$ contains a double bond, the large dipole moment expected from the formula $Me_2\bar{B}{=}\dot{N}Me_2$ is evidently very considerably reduced by unsymmetrical electron sharing in the sense B ⟶ N owing to the electronegativity difference between boron and nitrogen. The observed dipole moment [18] is only 1·40 ± 0·03 D (1·47 ± 0·06 D in $Me_2B{\cdot}NH_2$). Both $Ph_2B{\cdot}NMe_2$ and $Ph_2B{\cdot}NPh_2$ have such small dipole moments (1·6 and 1·0 D) that it is not obvious which end of the molecule is positive. Examination of *p*-tolyl derivatives shows that the *N*-methyl compounds have polarities of different sign from those of the *N*-aryl compounds: $Ph_2\overleftarrow{B{-}N}Me_2$ and $Ph_2\overrightarrow{B{-}N}Ph_2$. This reversal of polarity could be due to the electron-repelling effect of a methyl group, whereas a phenyl group can act as an electron-attractor in such a system. The change in moment, however, is rather large ($\Delta\mu = 2{\cdot}6$ D for the two compounds just mentioned). All the observed moments are consistent with only a small or zero net polarity for the B–N bond.

Phosphinoboranes.—The only monomeric phosphinoborane previously mentioned is the not very well characterized compound $Me_2B{\cdot}PH_2$, which was described as being sensitive to hydrolysis and methanolysis and slowly forming a polymer in ether solution.[5] We find, however, that in contrast to the tri-, tetra-, and poly-meric phosphinoboranes of the type $R_2B{\cdot}PR'_2$ (R = H or alkyl, R′ = alkyl or aryl), all the phosphinodi*aryl*boranes we have prepared are monomeric. In contrast to the aminoboranes, the monomeric phosphinodiarylboranes are relatively resistant to hydrolysis. The diarylphosphino-compounds are also unaffected by air.

(Diphenylphosphino)diphenylborane ($Ph_2B{\cdot}PPh_2$) was prepared by method (2), chlorodiphenylborane being added to an equimolar mixture of diphenylphosphine and triethylamine. Addition of diphenylphosphine to the other reactants gives the salt $[Et_3NH]^+[Ph_2BCl{\cdot}PPh_2]^-$, and diphenylphosphine and chlorodiphenylborane alone give a third compound $Ph_2\bar{B}Cl{-}\dot{P}HPh_2$. (Diphenylphosphino)diphenylborane is not only insoluble in, and undecomposed by, water but is so sparingly soluble in organic solvents that neither its molecular weight nor its dipole moment was measured. It is presumed to be monomeric or capable of reversible dissociation into monomer since it sublimed at 240° in a vacuum (dimer or trimer would contain 8 or 12 phenyl groups).

To obtain more soluble compounds, derivatives of di-*m*-tolylphosphine were prepared by a modification of reaction (1) in which the sodium derivative of di-*m*-tolylphosphine in tetrahydrofuran was added to chlorodiphenylborane in the same solvent:

$$(m\text{-}Me{\cdot}C_6H_4)_2PH + Na \xrightarrow{THF} Na^+(m\text{-}Me{\cdot}C_6H_4)_2P^- + \tfrac{1}{2}H_2 \xrightarrow{Ph_2BCl} Ph_2B{\cdot}P(C_6H_4Me\text{-}m)_2$$

The *m*-tolyl derivatives all had adequate solubility both for molecular-weight measurement in nitrobenzene and for dipole-moment measurement in benzene (in which they are sparingly soluble).

The diaryl(phosphino)boranes prepared are listed in Table 2.

The infrared spectra of the phosphorus compounds were very similar to those of their nitrogen analogues, and in all but one instance it was easy to distinguish the strong band almost certainly associated with stretching of the B–P bond. Since these bands (1400—1500 cm.$^{-1}$) are at higher frequencies than those of the B–N bands in most of the aminoboranes studied, in spite of the mass of a phosphorus being greater than that of a nitrogen atom, the boron–phosphorus bonds in the monomeric phosphinoboranes would appear to have pronounced double-bond character.

The monomeric phosphinoboranes might therefore be expected to have pronounced polar character, as indicated by the co-ordination formula (II). Moreover, since boron and phosphorus (and arsenic) have much the same electronegativity values (in the range

[18] Becher, *Z. anorg. Chem.*, 1952, **270**, 273.

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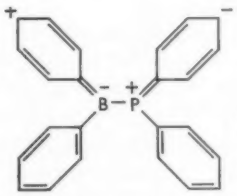
TABLE 2. *Diaryl(phosphino)boranes.*

Compound	B–P absorption frequency (cm.$^{-1}$)	Dipole moment (D)	Degree of association: Benzene Wt. %	Benzene *n*	Nitrobenzene Wt. %	Nitrobenzene *n*
$Ph_2B{\cdot}PEt_2$	1440 [b]	1·1	0·431	1·05	0·223	1·03
			0·801	1·12	0·509	1·12
			1·52	1·22	1·727	1·28
			1·96	1·54	2·466	1·39
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}PEt_2$	1412 [a]	0·7	0·172	1·01		
			0·283	1·12		
			0·885	1·16		
			1·571	1·27		
$Ph_2B{\cdot}PPh_2$	1445 [a]	(Not sufficiently soluble, see text)				
$Ph_2B{\cdot}P(C_6H_4Me\text{-}m)_2$	1482 [a]	2·2			0·348	1·00
					0·391	1·01
					0·477	0·89
$(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}P(C_6H_4Me\text{-}m)_2$	1487 [a]	2·9			0·472	1·11
					0·943	1·17
					1·266	1·03
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}P(C_6H_4Me\text{-}m)_2$	1480 [a] or 1425 [a]	0·6			0·421	0·97
					0·987	1·06
					1·19	1·15

[a] In KI disc. [b] In benzene solution.

1·9—2·1, however computed; see Pritchard and Skinner's review [19]), the moment indicated in (II) should not be reduced by bond polarization as in the aminoboranes (the electronegativity of nitrogen being about 3).

(II) (III)



(IV)

In fact, inspection of Table 2, with the effect of methyl and bromo-substituents on dipole moments in mind, shows that the moments of the phosphinoboranes are larger than those of the corresponding aminoboranes, and that the phosphino-group is the *negative* end of the dipole (III). From Table 2 the dipole moment of (III; Ar = R = Ph) must be about 2·5 D, that of (III; Ar = Ph, R = Et) being about 1·1 D and in the same direction.

This surprising result suggests that phosphorus is acting as a *weak* π-donor (to boron) in these compounds, possibly owing to an unfavourable relation between the " sizes " of boron 2*p*- and phosphorus 3*p*-orbitals. In all the diarylboranes some electron flow is to be expected from the aryl groups to the vacant boron 2*p*-orbital, and in $Ph_2B{\cdot}PEt_2$ this could perhaps account for the greater part of the observed dipole moment. Good evidence for such effects has been obtained from studies on the dipole moments of alkyl- and aryl-dihalogenoboranes.[20] Though the boron atom in a diaryl(diethylphosphino)-borane could thus be regarded as co-ordinatively saturated, or partly so, the phosphorus is not, and in fact the di*ethyl*phosphino-compounds add methyl iodide to form phosphonium salts $\{Ar_2B{\cdot}PEt_2Me\}I$.

In $Ph_2B{\cdot}PPh_2$ and related compounds the still larger moments would be due, in effect, to conjugation both between boron and aryl and between phosphorus and aryl, as shown in the " resonance " formula (IV). This formulation accounts in a qualitative way, not only for the observed dipole moments, but also for the lack of chemical reactivity, since both boron and phosphorus are co-ordinatively saturated (or partly so). Further, the

[19] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.
[20] Curran, McCusker, and Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5188.

charge separation between boron and phosphorus indicated in (IV) should result in B–P stretching force constants greater than would be expected for B–P single bonds, since the B–P bond would amount to a σ-bond possibly with a small π-component but with some electrostatic attraction in addition.

The relative importance of structures analogous to (IV) in the aminoboranes is, we suggest, much less because boron and nitrogen achieve co-ordinative saturation by formation of a B=N double bond.

TABLE 3. *Arsinodiarylboranes.*

Compound	B–As adsorption frequency (cm.$^{-1}$) (KI disc)	Dipole moment (D)	Degree of association			
			Benzene		Nitrobenzene	
			Wt. %	n	Wt. %	n
$Ph_2B{\cdot}AsPh_2$	1369	1·3	0·333	1·09	0·447	1·04
			0·715	1·26	0·734	1·05
			1·891	1·76	1·802	0·99
			2·891	1·95	2·598	1·06
$(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}AsPh_2$ ...	1439	2·1	0·691	0·94		
			1·23	0·99		
			2·41	1·14		
			3·33	1·37		
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}AsPh_2$ ...	1370	~0·4	0·704	1·04		
			1·29	1·12		
			2·44	1·31		
			2·98	1·38		

The reason for the phosphinodiarylboranes' being monomeric, when the series $R_2B{\cdot}PR'_2$ (R = H, alkyl) form trimers, tetramers, or polymers, thus lies in the boron atom in the diarylborane series being already co-ordinatively saturated (or nearly so) not by π-bonding with phosphorus but by π-bonding with the aryl groups.

Arsinoboranes.—These were prepared from the chlorodiarylborane and the sodium salt of the diarylarsine in tetrahydrofuran; they are listed in Table 3. Infrared spectra again resembled those of the nitrogen and phosphorus compounds, but the tetraphenyl compound $Ph_2B{\cdot}AsPh_2$ was very much more soluble than $Ph_2B{\cdot}PPh_2$ in organic solvents. The diaryl(arsino)boranes resembled the phosphino-analogues in their resistance to water or dilute acids or alkalis at 100°, but differed in their quantitative and analytically useful reaction with aqueous-alcoholic hydrogen peroxide at room temperature:

$$Ph_2B{\cdot}PAr_2 + H_2O_2 \longrightarrow 2PhOH + H_3BO_3 + Ar_2PO_2H$$
$$Ph_2B{\cdot}AsAr_2 + H_2O_2 \longrightarrow 2PhOH + 2ArOH + H_3BO_3 + H_3AsO_4$$

The B–As absorption bands are at rather lower frequencies than those of B–P bands in analogous compounds, and in the same region as B–N bands. The arsino-group is, as in the phosphinoboranes, the *negative* end of the dipole, the moments being rather less. We conclude that the electronic situation in the arsinoboranes resembles that in the phosphinoboranes, the smaller moments of the former being due to a smaller degree of electron transfer from arsenic to the aryl groups bound to it.

Though the σ-donor character of nitrogen, phosphorus, and arsenic towards boron diminishes in that order, it seems that the π-donor character diminishes even more rapidly.

EXPERIMENTAL

Microanalyses (C, H, and halogen) are by Mr. A. Wiper and Miss V. Conway, of these laboratories.

Combustion analyses often presented the difficulties, familiar with organoboron compounds, due to the retention of carbon as boron carbide in combustion residues, leading to erratic results for carbon. More reproducible results were generally obtained when smaller samples were burnt, and when the residue after combustion was heated with an oxygen-enriched flame.

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Compounds were in several instances identified by quantitative hydrolysis (for amino-) or oxidation reactions (for phosphino- and arsino-derivatives). Cryoscopic constants were determined by using biphenyl for benzene, and *p*-nitrotoluene for nitrobenzene.

Except in the case of one compound, for which refractivities were measured over a range of wavelengths, refractivities were measured at 6620 Å (Jena interference filter) and atom polarizations were taken as 10% of these refractivities.

Dipole moments were measured in benzene solution, total polarizations being derived by Halverstat and Kumler's method.[21] In spite of the apparent association of many of the compounds studied, as suggested by cryoscopic measurements, dielectric constant–weight fraction plots were always very nearly linear.

Infrared spectra were measured with a Grubb-Parsons GS2A grating spectrometer.

Chlorodiphenylborane, which was used in several preparations, has previously been described as a liquid; [22] we found it had m. p. 21·5—22·0°.

Aminodiphenylborane, $(Ph_2B{\cdot}NH_2)_2$.—Chlorodiphenylborane [22] [from diphenylborinic acid [23] and trichloroborane] (10 g., 0·05 mole) in ether (100 c.c.) was saturated with ammonia at room room temperature, and triethylamine (5·1 g., 0·05 mole) in ether (50 c.c.) was slowly added. The mixture was boiled under reflux for 1 hr., cooled, and filtered under nitrogen from triethylamine hydrochloride. The filtrate was evaporated; and the colourless *product*, crystallized from benzene, had m. p. 129—130° (3·6 g., 43%) (Found: C, 79·4; H, 6·7. $C_{12}H_{12}BN$ requires C, 79·9; H, 6·6%).

Dimethylaminodiphenylborane, $Ph_2B{\cdot}NMe_2$.—To a solution of monomeric dichlorodimethylaminoborane [24] (3·2 g., 0·025 mole) in benzene (50 c.c.) was slowly added phenylmagnesium bromide (0·05 mole) in ether. The mixture was evaporated and organic product extracted with hot benzene. Vacuum-distillation of the extract yielded a clear colourless liquid *product*, b. p. 102—104°/0·05 mm. (4·1 g., 81%) (Found: C, 80·8; H, 8·0. $C_{14}H_{16}BN$ requires C, 80·4; H, 7·6%).

Dimethylaminodi-p-*tolylborane*, $(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}NMe_2$, b. p. 110—112°/0·04—0·05 mm. (76%) [Found: C, 80·0; H, 8·6. $C_{16}H_{20}BN$ requires C, 81·1; H, 8·4%). By hydrolysis, found: $(p\text{-}Me{\cdot}C_6H_4)_2B$, 81·8, 80·5; Me_2N, 18·8, 18·3. $C_{16}H_{20}BN$ requires $(p\text{-}Me{\cdot}C_6H_4)_2B$, 81·5; Me_2N, 18·6%], and *di*-p-*bromophenyldimethylaminoborane*, $(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}NMe_2$, m. p. 39—40° (from benzene–hexane) (44%) (Found: C, 46·6; H, 3·7; Br, 43·9. $C_{14}H_{14}BBr_2N$ requires C, 45·8; H, 3·8; Br, 43·7%), were similarly prepared by using *p*-tolyl- and *p*-bromophenyl-magnesium bromide respectively.

(*Diphenylamino*)*diphenylborane*, $Ph_2B{\cdot}NPh_2$.—*Method* 1. Lithium diphenylamide in dry ether was slowly added to an equivalent quantity of chlorodiphenylborane in ether at −60°. The mixture was allowed to warm to room temperature and filtered under nitrogen, and the white *product* which resulted from removing solvent from the filtrate was crystallized from benzene; it had m. p. 148—150° (66%) (Found: C, 85·8; H, 6·1; B, 3·14. $C_{24}H_{20}BN$ requires C, 86·4; H, 6·0; B, 3·26%) [0·186 g. was warmed with aqueous acetone for a few minutes, and a slight excess of ethanolamine added. The reaction mixture was poured into water, and the solid collected, dried, and sublimed in a vacuum. The sublimate (0·093 g.) was identified (infrared spectrum) as diphenylamine, and the residue (0·132 g.) was similarly identified as 2-aminoethyl diphenylborinate ($C_{24}H_{20}BN$ requires 0·096 g. and 0·128 g. respectively)].

Method 2. Diphenylamine in benzene was added to a solution containing equivalent amounts of triethylamine and chlorodiphenylborane in the same solvent. The mixture was boiled under reflux for 30 min. and filtered under nitrogen from triethylamine hydrochloride (m. p. 255—256°), and the filtrate was concentrated to crystallization (61%). The infrared spectrum of the product was identical with that of the material prepared by method (1).

(*Di*-p-*tolylamino*)*diphenylborane*, $Ph_2B{\cdot}N(C_6H_4{\cdot}Me\text{-}p)_2$, m. p. 130—132° (from benzene–hexane) [Found: C, 85·3; H, 6·5. $C_{26}H_{24}BN$ requires C, 86·3; H, 6·8%. By hydrolysis, found: Ph_2B, 45·9; $(p\text{-}Me{\cdot}C_6H_4)_2N$, 54·9. $C_{26}H_{24}BN$ requires Ph_2B, 45·8; $(p\text{-}Me{\cdot}C_6H_4)_2N$, 54·2%] was prepared by methods (1) (53%) and (2) (57%).

Diphenylaminodi-p-*tolylborane*, $(p\text{-}CH_3{\cdot}C_6H_4)_2B{\cdot}NPh_2$.—This was prepared by method (2). The *product*, crystallized from benzene–hexane (67%, had m. p. 72—73° [Found: C, 89·9;

[21] Halverstat and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.
[22] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.
[23] Povlock and Lippincott, *J. Amer. Chem. Soc.*, 1958, **80**, 5409.
[24] J. F. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219.

H, 7·0. $C_{26}H_{24}BN$ requires C, 89·1; H, 7·0%). By hydrolysis, found: (p-Me·C_6H_4)$_2$B, 53·8, 53·7; Ph_2N, 46·8, 46·4. $C_{26}H_{24}BN$ requires (p-Me·C_6H_4)$_2$B, 53·4; Ph_2N, 46·6%].

(*Diethylphosphino*)*diphenylborane*, $Ph_2B{\cdot}PEt_2$.—n-Butyl-lithium (0·025 mole) in benzene was added to a solution of diethylphosphine [25] (2·3 g., 0·025 mole) in benzene at room temperature. Sufficient tetrahydrofuran was added to dissolve the pale yellow precipitate ($LiPEt_2$), and to this solution was slowly added chlorodiphenylborane (5 g., 0·025 mole) in benzene (50 c.c.). Water (100 c.c.) was added to the mixture. The benzene layer, when separated, dried ($MgSO_4$), and evaporated, gave a colourless *product*, m. p. 192° (from benzene) (5·3 g., 84%) (Found: C, 75·8; H, 7·9; B, 4·4; P, 12·0. $C_{16}H_{20}BP$ requires C, 75·6; H, 7·9; B, 4·25; P, 11·8%).

Di-p-*bromophenyl*(*diethylphosphino*)*borane*, (p-Br·C_6H_4)$_2$B·PEt_2, was similarly prepared from (di-p-bromophenyl)chloroborane, and crystallized from benzene–hexane; it had m. p. 202° (49%) (Found: C, 45·9; H, 4·3; Br, 38·1. $C_{16}H_{18}BBr_2P$ requires C, 46·5; H, 4·4; Br, 38·9%). Addition of methyl iodide to a solution of the phosphinoborane in benzene gave an immediate white precipitate of *methiodide*, m. p. 310—312° (decomp.) (Found: I, 23·1, 23·3. $C_{17}H_{21}BBr_2IP$ requires I, 22·9%).

(*Diphenylphosphino*)*diphenylborane*, $Ph_2B{\cdot}PPh_2$.—Chlorodiphenylborane (5 g.) in benzene (50 c.c.) was added at room temperature to a mixture of diphenylphosphine (4·2 g.) and triethylamine (2·5 g.) in benzene (50 c.c.). Part of the resulting thick white precipitate was dissolved by addition of water, and the rest was separated, washed several times with ether, and dried, and the *phosphinoborane* collected by sublimation (240°/10^{-3} mm.; 5·4 g., 61%) (Found: C, 78·9; H, 5·6. $C_{24}H_{20}BP$ requires C, 82·3; H, 5·7%). [0·1906 g. was warmed with aqueous-alcoholic hydrogen peroxide, and the phenol separated by steam distillation afforded tribromophenol, 0·348 g. ($C_{24}H_{20}BP$ requires 0·359 g.). Diphenylphosphinic acid (m. p. 195—196°) was isolated, but not quantitatively, from the steam-distillation residue].

This compound was also prepared by method (1), from the sodium derivative of diphenylphosphine and chlorodiphenylborane in 2,5-dioxahexane at −60°, but in lower yield (51%). The infrared spectrum of the water-insoluble solid product showed the presence of P–H bonds. The pure product was separated by vacuum-sublimation.

Chloro(*diphenylphosphino*)*diphenylborane*, $BClPh_2{\cdot}PHPh_2$.—Diphenylphosphine (4·2 g.) in benzene (25 c.c.) was slowly added to chlorodiphenylborane (5 g.) in benzene (20 c.c.). The white crystalline and very hydroscopic *adduct* (7·3 g., 75%), m. p. 83—85°, was filtered off (Found: Cl, 9·04, 9·08. $C_{24}H_{21}BClP$ requires Cl, 9·18%).

Triethylammonium Chloro(*diphenylphosphino*)*diphenylborate*, $Et_3NH^+\ BPh_2Cl{\cdot}PPh_2^-$.—Diphenylphosphine (4·2 g.) in benzene (25 c.c.) was added to a mixture of chlorodiphenylborane (5 g.) and triethylamine (2·5 g.) in benzene (25 c.c.). The colourless precipitated *salt* (77%), m. p. 152—153°, was collected (Found: C, 72·4; H, 7·7; B, 3·71; Cl, 6·9; Et_3N, 19·8. $C_{30}H_{36}BClNP$ requires C, 73·5; H, 7·4; B, 3·24; Cl, 7·1; Et_3N, 20·1%).

(*Di*-m-*tolylphosphino*)*diphenylborane*, $Ph_2B{\cdot}P(C_6H_4{\cdot}Me\text{-}m)_2$.—A solution of the sodium derivative of di-m-tolylphosphine (4·2 g.) in tetrahydrofuran (20 c.c.) was added to chlorodiphenylborane (4·0 g.) in ether (20 c.c.) at room temperature. Most of the solvent was then removed by evaporation, and the residue was extracted with hot benzene. Evaporation of the benzene solution gave the colourless *phosphinoborane* (5·1 g., 67%), m. p. 123—124° (Found: C, 81·9; H, 6·3. $C_{26}H_{24}BP$ requires C, 82·4; H, 6·4%).

Di-m-*tolylphosphinodi*-p-*tolylborane*, (p-$CH_3{\cdot}C_6H_4$)$_2$B·P($C_6H_4{\cdot}CH_3$-m)$_2$, m. p. 257—258° (from benzene–hexane; 67%) (Found: C, 80·9; H, 6·9. $C_{28}H_{28}BP$ requires C, 82·8; H, 6·9%), and *di*-p-*bromophenyldi*-m-*tolylphosphinoborane*, (p-BrC_6H_4)$_2$B·P(C_6H_4Me-m)$_2$, m. p. 281° (from benzene–hexane; 66%) (Found: C, 60·2; H, 4·1; Br, 30·1. $C_{26}H_{22}BBr_2P$ requires C, 58·1; H, 4·1; Br, 29·9%), were similarly prepared from the sodium derivative of di-m-tolylphosphine and the appropriate chlorodiarylborane.

(*Diphenylarsino*)*diphenylborane*, $Ph_2B{\cdot}AsPh_2$.—Diphenylarsine (5·8 g., 0·025 mole) was converted into its sodium derivative by reaction with excess of sodium wire in tetrahydrofuran (50 c.c.) at room temperature. The ruby-red solution was decanted under nitrogen from the excess of sodium and slowly added to chlorodiphenylborane (5 g., 0·025 mole) in tetrahydrofuran at −60°, the red colour being immediately discharged. The mixture was allowed to warm to room temperature, then filtered under nitrogen from precipitated sodium chloride, and the

[25] Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 704.

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filtrate was evaporated. The residue, crystallized from benzene, gave the colourless *arsinoborane* (5·8 g., 57%), m. p. 202—204° (Found: C, 72·6; H, 5·1. $C_{24}H_{20}AsB$ requires C, 73·1; H, 5·1%) [0·0944 g. was boiled (10 min.) with aqueous-alcoholic hydrogen peroxide; and the phenol, separated by steam-distillation, was converted into tribromophenol, 0·2966 g. ($C_{24}H_{20}AsB$ requires 0·3190 g.). The aqueous residue was boiled a few minutes with a trace of platinum black to remove excess of peroxide, then filtered, and boric and arsenic acid were estimated volumetrically (Found: B, 3·61; As, 18·6. $C_{24}H_{20}AsB$ requires B, 3·68; As, 19·0%)].

The same compound (identical mixed m. p. and infrared spectrum) was obtained in 67% yield by the triethylamine method.

(*Diphenylarsino*)*di*-p-*tolylborane*, (p-$Me{\cdot}C_6H_4)_2B{\cdot}AsPh_2$, (69%), m. p. 224—225° (from benzene–hexane) (Found: C, 73·6; H, 5·6. $C_{26}H_{24}AsB$ requires C, 74·0; H, 5·7%), and the p-*bromophenyl analogue*, (p-$BrC_6H_4)_2B{\cdot}AsPh_2$, m. p. 244—245° (67%) (from benzene–hexane) (Found: C, 52·3; H, 3·4. $C_{24}H_{18}AsBBr_2$ requires C, 51·2; H, 3·3%), were both prepared from the sodium derivative of diphenylarsine and the appropriate chlorodiarylborane.

The authors thank the Department of Scientific and Industrial Research for a maintenance grant (to J. G. L.), Borax Consolidated Ltd. for a gift of trimethoxyboroxine and Dr. G. Kohnstam for comments.

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[*Received, August 17th*, 1960.]

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204. *Naturally Occurring Quinones. Part V.*[1] *Spinochromes E and N.*

By J. SMITH and R. H. THOMSON.

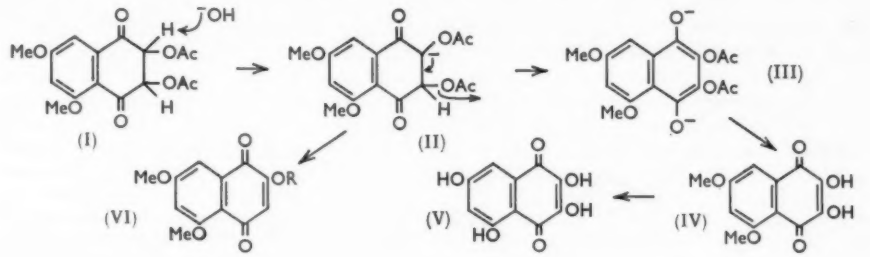
The structure of spinochrome N, 2,3,5,7-tetrahydroxy-1,4-naphthaquinone, is confirmed by synthesis. Spinochrome E is 2,3,5,6,7,8-hexahydroxy-1,4-naphthaquinone.

ONE of the many unusual features of sea urchins is the presence of polyhydroxynaphthaquinones (spinochromes) in the spines and test (shell) of many species. Although most work on the isolation of these pigments has been limited to the calcified regions of the animals, the occurrence of spinochromes in the internal organs and tissues is not excluded. In *Diadema antillarum* Philippi, for example, a naphthaquinone pigment is distributed generally throughout the animal.[2] This may be the case in other species and is probably significant. Although little is known of the biological function of these pigments some progress is now being made,[3] and it is desirable that their chemical structures should be more firmly established. About a dozen spinochromes are known,[4] but some of the structures put forward are not securely based, and none has been synthesised. In this paper we describe a synthesis of spinochrome N and put forward a structure for spinochrome E.

Spinochrome N.[5]—This pigment was isolated from the dark green spines of *Hemicentrotus pulcherrimus* (Ag.)[6] and the dark violet spines of *Anthocidaris crassispina* (Ag.)[7] by Kuroda and her co-workers, who proposed structure (V).[8] This has recently been supported[9] by oxidative degradation of its tetramethyl ether to 3,5-dimethoxyphthalic

[1] Part IV, Lovie and Thomson, *J.*, 1961, 485.
[2] Millott, *Proc. Zool. Soc. Lond.*, 1957, **129**, 263.
[3] Millott and Yoshida, *J. Exp. Biol.*, 1957, **34**, 394.
[4] Thomson, " Naturally Occurring Quinones," Butterworths, London, 1957.
[5] For nomenclature see ref. 4.
[6] Kuroda and Iwakura, *Proc. Imp. Acad.* (*Tokyo*), 1942, **18**, 74.
[7] Kuroda and Koyasu, *Proc. Imp. Acad.* (*Tokyo*), 1944, **20**, 23.
[8] A full account is given by Okajima, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1959, **53**, 356.
[9] Kuroda and Okajima, *Proc. Japan Acad.*, 1958, **34**, 616.

acid, and is now confirmed by synthesis. By the general procedure [10] for preparation of 2,3-dihydroxy-1,4-naphthaquinones, 5,7-dimethoxy-1,4-naphthaquinone was converted into 2,3-dihydroxy-5,7-dimethoxy-1,4-naphthaquinone (IV). Treatment of this with



diazomethane gave a tetramethoxyquinone identical with spinochrome N tetramethyl ether, and demethylation with aluminium chloride–sodium chloride afforded spinochrome N.

The formation of the dihydroxyquinone (IV) by aeration of the diacetate (I) in alkaline solution did not proceed smoothly and the yield was poor. Best results were obtained when the reaction was stopped before all the diacetate had disappeared, but even then a mixture was produced from which a monohydroxydimethoxyquinone was isolated. Larger amounts of the latter were isolated if either the reaction time or the alkali concentration was increased, probably owing to removal of the desired dihydroxyquinone by oxidative degradation. The monohydroxy-derivative was shown to have structure (VI; R = H) by treatment with methanolic hydrochloric acid which gave 2,5,7-trimethoxy-1,4-naphthaquinone (flaviolin trimethyl ether). The relative difficulty in obtaining the quinone (IV) from the diacetate (I), in comparison with previous examples,[10] may be attributed to the presence of two methoxyl groups in conjugation with the carbonyl group at position 4. This arrangement should assist initial proton abstraction from position 2 and subsequent elimination of acetate anion (see II), leading to the monohydroxyquinone (VI; R = H). The latter step competes with the formation of the dienol anion (III) which is required for the production of the dihydroxyquinone (IV).

Spinochrome E.[11]—This quinone occurs, with several others, in Mediterranean specimens of *Paracentrotus lividus* (Lam.) [12] and was recently isolated by Yoshida [13] from the test and spines of *Psammechinus miliaris* (Gmelin) (it is also present in the coelomic fluid of this species). In contrast to other spinochromes this one is insoluble in ether and has a very

high fusion point (>350°),[11] but the usual polyhydroxynaphthaquinone structure is apparent from its alkali-solubility, reversible reduction with dithionite, and ultraviolet- and visible-light absorption.[11,12]

The sample of spinochrome E, kindly supplied by Dr. M. Yoshida, had been crystallised from acidified (HCl) methanol and contained chlorine (3·3%). Nitrogen (2·3%) was also present which may have originated from the pyridine used in the purification procedure or may have been associated with the pigment *in vivo* as the initial crude material is soluble

[10] Garden and Thomson, *J.*, 1957, 2483.
[11] Smith and Thomson, *Tetrahedron Letters*, 1960, No. 1, 10.
[12] Lederer, *Biochim. Biophys. Acta*, 1952, **9**, 92.
[13] Yoshida, *J. Mar. Biol. Assoc. U.K.*, 1959, **38**, 455.

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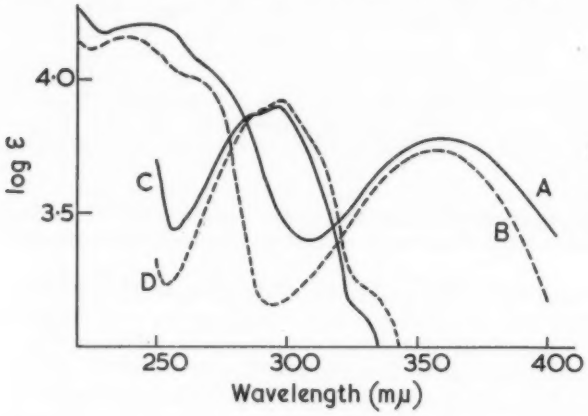
in hydrochloric acid. After purification *via* the acetate the quinone gave satisfactory analyses for a formula $C_{10}H_6O_8$. Since it formed a hexa-acetate, which on reductive acetylation gave a leuco-octa-acetate, all the oxygen atoms are accounted for, and moreover the ultraviolet spectra of these two compounds are very similar to the corresponding derivatives of spinazarin (2,3,5,8-tetrahydroxy-1,4-naphthaquinone) (see Figure). Spinochrome E is thus the hexahydroxynaphthaquinone (VII). (Tautomeric structures are not



(A) *Spinochrome E hexa-acetate*, (B) *2,3,5,8-tetra-acetoxy-1,4-naphthaquinone, in methanol*; (C) *spinochrome E leuco-octa-acetate*; (D) *1,2,3,4,5,8-hexa-acetoxynaphthalene, in chloroform.*

ruled out on this evidence but are much less probable.) This structure is consistent with its colour reactions,[11] low solubility, and high melting point. On treatment with diazomethane it gave a tetramethyl ether which, from its colour reactions and the absence of hydroxyl absorption in the 3 μ region, contains no β-hydroxyl groups and therefore has structure (VIII).

Mukai [14] has shown recently that namakochrome, the prosthetic group of a purple chromoprotein present in the holothuroid *Polycheira rufescens* (Brandt), is a pentahydroxymonomethoxynaphthaquinone. It gives a trimethyl ether with diazomethane which we find to be identical with spinochrome E tetramethyl ether (VIII). Hence namakochrome is a mono-β-methyl ether of spinochrome E. The occurrence of this pigment in a holothuroid and the recent discovery [15] of polyhydroxyanthraquinones in crinoids indicate that polyhydroxyquinones may be fairly widely distributed in echinoderms, but their origin remains obscure. Their close structural relationship to acetate-derived fungal quinones (*e.g.*, flaviolin) suggests that they might be biosynthesised from C_2 units but there is no evidence, as yet, which shows that this metabolic pathway operates in animals.

Experimental

5,7-Dimethoxy-1,4-naphthaquinone.—A suspension of 5,7-dihydroxy-1,4-naphthaquinone [10] (1 g.) in chloroform (35 ml.) was vigorously shaken with silver oxide (5 g.) and methyl iodide (4 ml.). Two additions of silver oxide (2·5 g.) and methyl iodide (2 ml.) were made at intervals of 2 hr. and the shaking was continued overnight. The *dimethoxyquinone* crystallised from light petroleum (b. p. 100—120°) in light-yellow flakes, m. p. 146° (760 mg.) (Found: C, 65·9; H, 4·6. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6%).

2,3-Dihydroxy-5,7-dimethoxy-1,4-naphthaquinone (IV).—30% Hydrogen peroxide (0·42 ml.) and 10% aqueous sodium carbonate (0·90 ml.) were added to a solution of 5,7-dimethoxy-1,4-naphthaquinone (400 mg.) in alcohol (10 ml.) at 47°. The temperature rose to 50° and after being stirred at this temperature for 5 min. the mixture was cooled, diluted with water, and set

[14] Mukai, *Mem. Fac. Sci. Kyushu Univ., Series C, Chem.*, 1958, **3**, No. 2, 29; *Bull. Chem. Soc. Japan*, 1960, **33**, 453, 1234; personal communication.
[15] Sutherland and Wells, *Chem. and Ind.*, 1959, 291.

aside on ice. The *epoxide*, which separated, crystallised from light petroleum (b. p. 100—120°) in straw-coloured needles, m. p. 136° (215 mg.) (Found: C, 61·4; H, 4·4. $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3%). When the epoxide (220 mg.) was stirred for 15 min. in ice-cold acetic anhydride (2·4 ml.) containing concentrated sulphuric acid (0·2 ml.) it gradually dissolved and then 2,3-*diacetoxy*-1,2,3,4-*tetrahydro*-5,7-*dimethoxy*-1,4-*dioxonaphthalene* (I) separated. Crystallised from a large volume of ethyl acetate (charcoal), it had m. p. 194—196° (decomp. >180°) (160 mg.) (Found: C, 56·8; H, 4·9. $C_{16}H_{16}O_8$ requires C, 57·1; H, 4·8%). The diacetate (230 mg.) was triturated with ice-cold N-sodium hydroxide (7 ml.), the initial transient grey colour changing rapidly through green to deep blue. After 2 min. the solution was filtered quickly and acidified (*ca.* 20 mg. of undissolved starting material was recovered), and then diluted with water and extracted with ether (3 × 10 ml.). Repeated extraction with chloroform then yielded the *dihydroxyquinone* (IV) which crystallised from methanol in long orange-red needles, m. p. 225° (40—60 mg.) (Found: C, 56·9; H, 4·2. $C_{12}H_{10}O_6$ requires C, 57·6; H, 4·0%), and gave a violet solution in aqueous sodium hydroxide. The *diacetate* crystallised from light petroleum (b. p. 100—120°) in yellow needles, m. p. 182° (Found: C, 57·2; H, 4·2. $C_{16}H_{14}O_8$ requires C, 57·4; H, 4·2%).

2,5,7-*Trimethoxy*-1,4-*naphthaquinone*.—The combined ethereal extracts from three of the above reactions were kept at room temperature until an orange solid was deposited; complete evaporation of the solvent left only a black residue. The orange material was crystallised once from methanol (charcoal), and a portion of the product (140 mg.) was boiled under reflux with 3% methanolic hydrogen chloride (5 ml.) for 15 min. The small yellow needles which separated on cooling were dissolved in benzene (charcoal), chromatographed on alumina according to Davies *et al.*,[16] and crystallised from benzene–light petroleum (b. p. 50—60°) to give golden needles of 2,5,7-trimethoxy-1,4-naphthaquinone, m. p. and mixed m. p. with tri-*O*-methylflaviolin, 187° (mixed m. p. with 3,5,7-trimethoxy-1,4-naphthaquinone, 170°) (42 mg.) (Calc. for $C_{13}H_{12}O_5$: C, 62·9; H, 4·9. Found: C, 62·8; H, 4·9%).

2,3,5,7-*Tetramethoxy*-1,4-*naphthaquinone*.—An ethereal solution of diazomethane (from 2 g. of nitrosomethylurea) was added to an ice-cold suspension of 2,3-dihydroxy-5,7-dimethoxy-1,4-naphthaquinone (150 mg.) in ether (15 ml.) and kept at 0° for 30 min. After 2 hr. at room temperature the flocculent precipitate of *tetramethyl ether*, which had replaced the starting material, was collected and crystallised from light petroleum (b. p. 100—120°) in long thin yellow needles, m. p. 131° (unaltered on admixture with spinochrome N tetramethyl ether, m. p. 130°) (110 mg.) (Found: C, 60·4; H, 4·8. $C_{14}H_{14}O_8$ requires C, 60·4; H, 5·1%). The infrared spectra (KBr disc) of the " natural " and the synthetic material were identical.[8]

2,3,5,7-*Tetrahydroxy*-1,4-*naphthaquinone*.—2,3-Dihydroxy-5,7-dimethoxy-1,4-naphthaquinone (230 mg.) was stirred in a melt of anhydrous aluminium chloride (8 g.) and sodium chloride (1·4 g.) at 180° for 2 min. After cooling somewhat, the molten mixture was poured into 5N-hydrochloric acid (120 ml.). A dark solid (with bright-red inclusions) separated and was extracted with chloroform; the aqueous solution was extracted with ether and the combined, dried ($MgSO_4$) extracts were evaporated. The residue sublimed at >130°/6 × 10^{-7} mm. and the sublimate was taken up in the minimum amount of ether. Addition of light petroleum (b. p. 50—60°) precipitated a bright red, amorphous material which was throughly washed with light petroleum (b. p. 50—60°) containing a little ether, and crystallised from methanol forming small, red needles (7—8 mg.) of 2,3,5,7-*tetrahydroxy*-1,4-*naphthaquinone* which gradually decomposed at >260° (Found: C, 54·2; H, 2·6. $C_{10}H_6O_6$ requires C, 54·05; H, 2·7%). The tetrahydroxyquinone gave a yellowish-green solution in aqueous sodium hydroxide, a green solution in aqueous sodium hydrogen carbonate, and a transient green ferric colour in methanol. Its infrared, ultraviolet, and visible absorption curves were identical with those of spinochrome N.[8]

Spinochrome E.—The sample, previously crystallised [13] from methanol containing hydrochloric acid, was acetylated and then hydrolysed with boiling methanolic sulphuric acid. It separated on dilution as brownish-red needles, which blackened without melting >300° (Found: C, 47·0; H, 2·5. $C_{10}H_6O_8$ requires C, 47·2; H, 2·4%). The infrared spectra of samples obtained from *Psammechinus miliaris* [13] and *Paracentrotus lividus* [13] were virtually identical and showed only minor discrepancies. The pure material showed $\nu_{max.}$ (in KBr) at 3520, 3150, 1652sh, 1629, 1586, 1490, 1456, 1344, 1274, 1181, 1062w, 1041w, 992, 839, 803, 766, 716 $cm.^{-1}$. The *hexa-acetate* was obtained by boiling the pigment (96 mg.) in acetic anhydride (2 ml.)

[16] Davies, King, and Roberts, *J.*, 1955, 2782.

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containing one drop of concentrated sulphuric acid; it (160 mg.) crystallised from ethanol in yellow needles, m. p. 192° (Found: C, 52·6; H, 3·7; Ac, 50·2. $C_{32}H_{18}O_{14}$ requires C, 52·1; H, 3·6; Ac, 51·0%). The hexa-acetate (100 mg.) was boiled in acetic anhydride (2·3 ml.) with zinc dust (200 mg.) and a trace of triethylamine for 10 min. to give the *leuco-octa-acetate* which formed needles (from glacial acetic acid), m. p. 265° (decomp.) (53 mg.) [Found: C, 53·0; H, 4·0; Ac, 57·1%; *M* (ebullioscopic in benzene), 556. $C_{28}H_{24}O_{16}$ requires C, 52·7; H, 4·05; Ac, 58·1%; *M*, 592].

Spinochrome E Tetramethyl Ether (cf. Kuroda [17]).—Spinochrome E (32 mg.) was spread on six watch-glasses and treated dropwise with ethereal diazomethane until there was no further reaction. The residue was washed with small amounts of ether and crystallised from methanol, forming long, brown, needles, m. p. 185° (8 mg.) (Found: C, 54·1; H, 4·6. Calc. for $C_{14}H_{14}O_8$: C, 54·2; H, 4·5%). This ether gave a brown ferric reaction, a violet *solution* with methanolic lead acetate, and a blue-violet solution in aqueous sodium hydroxide, but was not extracted from ethereal solution by aqueous sodium hydrogen carbonate. On prolonged contact with this reagent a purple solution is obtained (spinazarin 2,3-dimethyl ether behaves similarly). The m. p. was not depressed on admixture with namakochrome trimethyl ether and the infrared spectra of the specimens were identical.[14]

We are greatly indebted to Drs. M. Yoshida, E. Lederer, M. Okajima T. Mukai, and J. E. Davies for specimens of natural products and derivatives, to Dr. V. C. Farmer for some of the infrared data, and Imperial Chemical Industries Limited, Nobel Division, for the molecular-weight determination. One of us (J. S.) thanks the Executive Committee of the Shirley Institute for the award of a Fellowship.

THE UNIVERSITY, OLD ABERDEEN, SCOTLAND. [*Received, August* 31*st*, 1960.]

[17] Kuroda, *Proc. Imp. Acad.* (*Tokyo*), 1942, **18**, 69.

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205. *Aromatic Reactivity. Part XV.*[1] *Biphenyl and Naphthalene in Detritiation.*

By C. EABORN and R. TAYLOR.

We have measured the rates of detritiation of [2-, 3-, and 4-$^3H_1$]biphenyl and of [α- and β-$^3H_1$]naphthalene in trifluoroacetic acid containing aqueous sulphuric acid or aqueous perchloric acid. The 2- and the 4-position of biphenyl are about equally reactive in this hydrogen-exchange, and markedly more reactive than a single position in benzene, while the 3-position is somewhat less reactive than a single position in benzene. The α-position of naphthalene is more reactive than the β-position, which is about as reactive as the 4-position of biphenyl. The partial rate factors for the 4-position of biphenyl and the 2-position of naphthalene are compared with those in other electrophilic aromatic substitutions; it is shown that activation of these positions relative to activation of the *para*-position of toluene depends greatly on the electron-demand, but it is argued that there is nothing qualitatively abnormal about activation in biphenyl and naphthalene.

WE have measured the rates of detritiation at 25·0° of monotritiated biphenyls and naphthalenes in media of the composition $CF_3{\cdot}CO_2H$ (95·31)–H_2O (2·21)–H_2SO_4 (2·48) and $CF_3{\cdot}CO_2H$ (92·04)–H_2O (5·45)–$HClO_4$ (2·51) (the figures denote mole-percentages) in which we previously studied detritiation of alkylbenzenes.[2] The values of the first-order rate constants, $k_{ex.}$, for the detritiation, are given in Table 1, along with the rates, *f*, relative to that for detritiation of [$^3H_1$]benzene, figures for [*p*-$^3H_1$]toluene being included for comparison. With the medium containing sulphuric acid, it was necessary to measure the rate of sulphonation, $k_{sulph.}$, of biphenyl and naphthalene, since sulphonation, whether

[1] Part XIV, Eaborn and Waters, *J.*, 1961, 542.
[2] Eaborn and Taylor, *J.*, 1961, 247.

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at a tritiated position or not, results in a loss of tritium, and $k_{sulph.}$ must be subtracted from the apparent exchange rate, $k_{obs.}$, to give the value of $k_{ex.}$ (see refs. 2 and 3). Sulphonation accounts for about 9% of the apparent exchange rate with [2- and 4-$^3H_1$]biphenyl,

TABLE 1. *Detritiation at 25·0°.*[a]

	$CF_3{\cdot}CO_2H$–H_2O–H_2SO_4[b] (95·31 : 2·21 : 2·48)				$CF_3{\cdot}CO_2H$–H_2O–$HClO_4$ (92·04 : 5·45 : 2·51)	
	$10^7k_{obs.}$	$10^7k_{sulph.}$	$10^7k_{ex.}$	f	$10^7k_{ex.}$	f
[$^3H_1$]Benzene[b]	3·74	<0·15	3·6	1	14·3	1
[p-$^3H_1$]Toluene[b]	2552	26	2526	702	4480	313
[2-$^3H_1$]Biphenyl	525	48	477	133	748	52
[3-$^3H_1$]Biphenyl	—	—	—	—	9·8	0·68
[4-$^3H_1$]Biphenyl	563	48	515	143	748	52
[α-$^3H_1$]Naphthalene	3990	104	3886	1079	5300	370
[β-$^3H_1$]Naphthalene	560	104	456	127	885	62

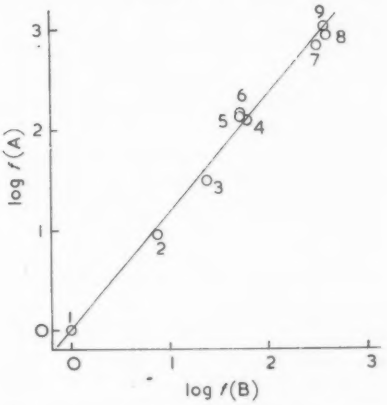
[a] Rate constants in sec.$^{-1}$. [b] See ref. 2.

and for about 3% with [α-$^3H_1$]naphthalene, but for about 19% with [β-$^3H_1$]naphthalene. [3-$^3H_1$]Biphenyl was not studied in this medium, but in a medium somewhat stronger in sulphuric acid [$CF_3{\cdot}CO_2H$ (85·08)–H_2O (6·42)–H_2SO_4 (8·50)] the value of $k_{sulph.}$ (341 × 10^{-7} sec.$^{-1}$) represented 97% of $k_{obs.}$ (353 × 10^{-7} sec.$^{-1}$), and the resulting figure for $k_{ex.}$ (12 × 10^{-7} sec.$^{-1}$) may be used only to conclude that exchange is slower than with [$^3H_1$]benzene (for which $k_{ex.} = 30 \times 10^{-7}$ sec.$^{-1}$), the value of f (0·4) possibly being in error by as much as ±100%. (In this medium $f_p^{Me} = ca.$ 540.) The exchanges in $CF_3{\cdot}CO_2H$–H_2O–$HClO_4$ were apparently free from interfering side-reactions.

Plot of (A) log f *in* $CF_3{\cdot}CO_2H$–H_2O–H_2SO_4 *against* (B) log f *in* $CF_3{\cdot}CO_2H$–H_2O–$HClO_4$.

Points:

1, [$^3H_1$]C_6H_5.
2, [m-$^3H_1$]C_6H_4Me.
3, [m-$^3H_1$]$C_6H_4Bu^t$.
4, [β-$^3H_1$]$C_{10}H_7$.
5, [2-$^3H_1$]$C_{12}H_9$.
6, [4-$^3H_1$]$C_{12}H_9$.
7, [p-$^3H_1$]C_6H_4Me.
8, [p-$^3H_1$]$C_6H_4Bu^t$.
9, [α-$^3H_1$]$C_{10}H_7$.



The results constitute the first reports of accurate partial rate factors for hydrogen-exchange at the several positions in biphenyl and naphthalene. The reactivities of the positions relative to one another have been measured for deuteration in $CF_3{\cdot}CO_2D$–CCl_4–D_2SO_4,[4] and the results are consistent with ours. (Rates relative to a single position in benzene can only be obtained from the deuteration results[4] by unsatisfactory extrapolations based on assumed dependences of rate on acidity function, and may be considerably in error.) The main features of our results are as follows:

(i) The spread of rates depends markedly on the medium, as with alkylbenzenes.[2,3,5] There is an approximate linear free-energy relation between the results in the two media (see Figure). (The line is drawn to pass between all the points. A good straight line

[3] Eaborn and Taylor, *J.*, 1960, 3301.
[4] Dallinga, Verrijn Stuart, Smit, and Mackor, *Z. Elektrochem.*, 1957, **61**, 1019.
[5] Eaborn and Taylor, *Chem. and Ind.*, 1959, 949.

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may be drawn to pass through the origin and the points for the alkylbenzenes, and the points for the naphthalene and biphenyl systems then fall to the left. This is what would be expected if the naphthalene and biphenyl systems respond more effectively to the increased electron-demand in $CF_3 \cdot CO_2H–H_2O–H_2SO_4$ which is indicated by the greater spread of rates in the medium. Discussion below is relevant to this point.)

(ii) The 2- and the 4-position of biphenyl are equally reactive. Since primary steric effects are unimportant in detritiation,[6] this result is probably a true reflection of the relative electronic activation at the positions, and is in agreement with Dewar's simple estimates of localization energies,[7,8] but not with more complicated calculations of localization energies,[9–11] with calculations by the self-consistent-field method of the energies required to convert the hydrocarbon ArH into the ion ArH_2^+,[4] or with free-valence numbers,[9] all of which assign a distinctly higher reactivity to the 2-position. The small deactivation of the 3-position disagrees with some calculations,[4,12] but agrees with others,[9] and also with experimental results in protodesilylation,[13] mercuridesilylation,[13] bromodesilylation,[13] and ionic bromination.[14]

(iii) The α-position of naphthalene is considerably more activated than the β-position, in agreement with calculations.[4,7–10] The β-position is roughly as reactive as the 4-position of biphenyl, being slightly more or less reactive depending on the medium. Calculations indicate that the β-position should be less reactive than the 4-position of biphenyl,[4,8–10] and this is the case in protodesilylation,[15] mercuridesilylation,[15] and protodegermylation [16] (all reactions which seem to make relatively small demands on electromeric effects of substituents), but in bromodesilylation the positions are equally reactive; [15] in nitration the β-position of naphthalene may be more reactive than the 4-position of biphenyl,[8] though there is conflicting experimental information on the partial rate factors for biphenyl in this reaction.[17]

(iv) The values of $(\log f_p^{Me})/(\log f_p^{Ph})$ are in line with the observation that this ratio shows a general tendency to fall from reaction to reaction as f_p^{Me} rises,[13] probably as the electron-demand rises and calls forth increasingly the $+E$ effect of the *p*-Ph group.[13,14]

TABLE 2.

Reaction	f_p^{Me}	$\log f_p^{Me}/\log f_p^{Ph}$	Reaction	f_p^{Me}	$\log f_p^{Me}/\log f_p^{Ph}$
Protodestannylation [1] ...	5·6	3·0	Ionic bromination [14]	59	1·48
Protodegermylation [16] ...	14	2·66	Detritiation	313	1·45
Protodesilylation [13]	18	2·82	Detritiation	702	1·32
Mercuridesilylation [15] ...	17·5	2·40	Molec. chlorination [18, 19] ...	820	1·05
Nitration [8, 14]	58	1·70			

Table 2 illustrates this. The results confirm the observation [13] that no single substituent constant can satisfactorily represent the effect of a *p*-Ph group in electrophilic aromatic substitution.*

(v) The values of the ratio $(\log f_p^{Me})/(\log f_{3,4}^{C_6H_4})$ are lower than for the other reactions

* The absolute deviation of the *p*-Ph group from a $(\log f)$–σ^+ plot may be no greater than for many other substituents, but the deviation relative to the value of σ^+, which is important in a detailed analysis of the effect of a group, is abnormally large, as discussed below.

[6] R. Baker, unpublished work.
[7] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3337.
[8] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[9] Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.
[10] Mason, *J.*, 1959, 1233.
[11] R. D. Brown, *Experientia*, 1950, **6**, 376; *J. Amer. Chem. Soc.*, 1953, **75**, 4077.
[12] Dewar, *J.*, 1952, 3544.
[13] Deans, Eaborn, and Webster, *J.*, 1959, 3031.
[14] de la Mare and Hassan, *J.*, 1957, 3004.
[15] Eaborn, Lasocki, and Webster, *J.*, 1959, 3034.
[16] Eaborn and Pande, *J.*, 1961, 297.
[17] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196.
[18] de la Mare, Hall, Harris, and Hassan, *J.*, 1958, 1086.
[19] H. C. Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.

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for which it is known, with the exception of nitration,[8] the data for which appear anomalous.† Apart from this, the value of the ratio tends generally to fall as f_p^{Me} rises

TABLE 3.

Reaction	f_p^{Me}	$\log f_p^{Me}/\log f_{3,4}^{C_4H_4}$	Reaction	f_p^{Me}	$\log f_p^{Me}/\log f_{3,4}^{C_4H_4}$
Protodegermylation [18]	14	4·54	Detritiation	313	1·39
Protodesilylation [15] ...	21	3·96	Detritiation	702	1·32
Mercuridesilylation [15] ...	17·5	2·69	Nitration [8]	58	1·02

(Table 3), indicating that electron-release by the activating ring is called forth more strongly as the general electron-demand rises. The way in which this ratio varies suggests that there is no qualitative difference between the type of response of biphenyl and of naphthalene systems to electron-demand; a difference would not have been surprising in view of the fact that the two rings are coplanar in naphthalene but not in biphenyl.

The results confirm the observation [15] that no single substituent constant can satisfactorily represent the effect of the 3,4-C_4H_4 system in electrophilic aromatic substitution.

(vi) The ratio $(\log f_{2,3}^{C_4H_4})/\log f_{3,4}^{C_4H_4})$ has values of 1·44 and 1·43 in the detritiations. These are lower than the values in desilylations,[15] in which steric effects occur.

(vii) " Reactivity numbers," [8] Hückel localization energies,[10] and energies calculated for formation of the ions ArH_2^+ from the hydrocarbons ArH,[4] are all quantitatively inconsistent with the observed reactivities, in that plots of $\log f$ for the single positions of benzene, biphenyl, and naphthalene against the various sets of energies are far from linear.

Activation in Biphenyl and Naphthalene.—We conclude with a brief general comment on the nature of the activating influences of the *p*-Ph group and the 3,4-C_4H_4 system in electrophilic aromatic substitution. We have shown that the effects of these substituents relative to that of a *p*-Me group, vary markedly with the electron-demand, but we wish to stress that there is nothing abnormal about the substituents. Any apparent abnormality is largely a consequence of calculating partial rate factors relative to a single position in benzene, which is logical (since, by definition, polar effects are absent at such a position) but not essential; if, for example, we calculated rate factors, f', relative to the *meta*-position in chlorobenzene, there would be fairly small variation in $(\log f'_p{}^{Me})/(\log f'_p{}^{Ph})$ ratios.

It is instructive to use Yukawa and Tsuno's approach [20] to analysis of substituent effects in electrophilic substitutions.‡ These authors point out that the quantity σ_R, which is equal to $(\sigma^+ - \sigma)$, is a measure of the potential ability of a substituent to stabilize, by resonance effects, a centre of excess positive charge with which it is conjugated. (The values of σ^+ are those derived from solvolysis of αα-dimethylbenzyl chlorides in 90% aqueous acetone,[23] and values of σ are those derived from ionization of benzoic acids in water at 25°.[24]) They further point out that the extent to which resonance effects operate varies from reaction to reaction, and show that for a number of electrophilic reactions the relation $\log f = \rho(\sigma + r\sigma_R)$ is more satisfactory than either of the relations $\log f = \rho\sigma$ and $\log f = \rho\sigma^+$.[20] The value of r, which is a measure of the extent to which electromeric and possibly inductomeric effects of substituents are brought into play, has, by definition, a value of 1 for solvolysis of αα-dimethylbenzyl chlorides and of 0 for ionization of benzoic acids in water, and can have a range of values above zero in electrophilic reactions; for

† The factors $f_{3,4}^{C_4H_4}$ and $f_{2,3}^{C_4H_4}$ refer respectively to the 2- and the 1-position of naphthalene.

‡ An equivalent approach will be found in ref. 21. A related procedure, but applicable to reactions in which loss of resonance occurs on going from initial state to transition state, has been outlined by Dickinson and Eaborn.[22]

[20] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.
[21] Bekhum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.
[22] Dickinson and Eaborn, *J.*, 1959, 3036.
[23] H. C. Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.
[24] McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

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example, 2·29 in brominolysis of benzeneboronic acids,[20] 1·66 in molecular chlorination in acetic acid,[20] 0·90 for nitration in nitromethane or acetic acid,[20] 0·7 in protodesilylation,[1] and 0·4 in protodestannylation.[1]

The values of σ_R for the *p*-Ph group (−0·17) and the 3,4-C_4H_4 system (−0·177) are not particularly large (cf. −0·141 for *p*-Me and −0·510 for *p*-OMe), but because σ is so small in both cases the value of the sum $(\sigma + r\sigma_R)$ rises steeply with r as the following Table shows:

r	0	0·2	0·4	0·6	0·8	1·0	1·5
$\sigma + r\sigma_R$ for *p*-Ph	−0·01	−0·04	−0·078	−0·11	−0·15	−0·179	−0·26
$\sigma + r\sigma_R$ for 3,4-C_4H_4...	+0·042	+0·007	−0·029	−0·064	−0·100	−0·135	−0·223
$\sigma + r\sigma_R$ for *p*-Me	−0·170	−0·198	−0·226	−0·255	−0·283	−0·311	−0·381

If the Yukawa–Tsuno equation applied exactly, then as r varied from 0·2, to 0·6, to 1, to 2, the value of the ratio $(\log f_p^{Me})/(\log f_p^{Ph})$ would fall from 5, to 2·3, to 1·7, to 1·3. [If we reckoned rate factors relative to the *meta*-position of chlorobenzene, this would be equivalent to adding *ca.* −0·38 to each value of the sum $(\sigma + r\sigma_R)$, and the new sum would then appear less variable with r.] The effect of the 3,4-C_4H_4 system falls into the same pattern; the value of σ_R is rather similar to that for *p*-Ph, and if it is slightly greater, as it may be, then the sum $(\sigma + r\sigma_R)$ for 3,4-C_4H_4 can overtake that for *p*-Ph at high values of r. We do not suggest, of course, that the Yukawa–Tsuno approach to substituent effects has fundamental significance in its present state of refinement, or that wholly quantitative analysis of effects on individual groups is possible by its use, but it serves to interpret semi-quantitatively the variability of effects of *p*-Ph and 3,4-C_4H_4 substituents noted in Tables 2 and 3, and to illustrate that the response of these substituents to electron-demand is not, in absolute terms, abnormal.

Experimental

Materials.—Monotritiated biphenyls and naphthalenes were made by the usual method from 2-iodo-, 3-bromo, or 4-bromo-biphenyl or from α-bromo- or β-chloro-naphthalene;[2,3] the Grignard reagent from the last compound was prepared in tetrahydrofuran. Maximum activities (theoretical use of the tritiated water being assumed; see ref. 3) were 2 and 3 mc./g. for [α- and β-$^3H_1$]naphthalene, respectively, 5 mc./g. for the [$^3H_1$]biphenyls. (Actual activities might have been only one-quarter of these values.)

Exchange Measurements.—The media and general method for rate measurements were as previously described,[2,3] except that for the naphthalene compounds only 5 ml. of toluene were used in the extraction in order to give a more active extract. About 0·02—0·03 g. of the tritiated aromatic compound was used in about 7·5 g. of the reaction medium, the solution obtained being sufficient for 5 samples in sealed tubes.[3] In calculating "equilibrium" deflections, it was assumed that four positions were available for tritiation with [α-$^3H_1$]-naphthalene, 8 with the β-isomer, 6 with [2- and 4-$^3H_1$]biphenyl, and 10 with the 3-isomer (cf. ref. 2). (In all cases the "equilibrium" deflection would correspond to less than 3% of the tritium's remaining in the aromatic compound.)

Sulphonation.—The rates of sulphonation of biphenyl and naphthalene in $CF_3{\cdot}CO_2H$–H_2O–H_2SO_4 were measured by partition of the hydrocarbon and its sulphonic acid between hexane and water, followed by spectrophotometric determination of the concentration of the hydrocarbon in the hexane.[3] Wavelengths of 247, 255, 265, and 280 mμ were used for biphenyl, and of 266, 276, 290, and 295 mμ for naphthalene. The first-order rate constants for sulphonation fell slightly as reaction proceeded (as sulphuric acid was removed and water formed; cf. ref. 2), and initial rates are given in Table 1. The rates determined at the several wavelengths agreed to within ±4%.

We thank the Department of Scientific and Industrial Research for financial support, and the Chemical Society for a grant from the Research Fund.

The University, Leicester. [*Received, September 9th,* 1960.]

206. *The Formation and Thermodynamic Properties of Nitrous Acid Vapour.*

By P. G. Ashmore and B. J. Tyler.

The gas-phase equilibrium between nitric oxide, nitrogen dioxide, water, and nitrous acid has been studied at 20°, 40°, 60°, and 80° c. Values of $\Delta S°_{298}$ and $\Delta H°_{298}$ for the reaction $NO_2 + NO + H_2O \longrightarrow 2HNO_2$ have been calculated from the measured equilibrium constants, and used to evaluate the standard heat of formation and standard entropy of nitrous acid vapour.

When nitric oxide, nitrogen dioxide, and water vapour are mixed in the gas phase, nitrous and nitric acid vapours are formed. As dinitrogen tetroxide and dinitrogen trioxide are also present, the system can be represented by the following equilibria:

$$2NO_2 \underset{-1}{\overset{1}{\rightleftharpoons}} N_2O_4 \quad . . . . . (1)$$

$$NO + NO_2 \underset{-2}{\overset{2}{\rightleftharpoons}} N_2O_3 \quad . . . . . (2)$$

$$NO + NO_2 + H_2O \underset{-3}{\overset{3}{\rightleftharpoons}} 2HNO_2 \quad . . . . . (3)$$

$$3NO_2 + H_2O \underset{-4}{\overset{4}{\rightleftharpoons}} 2HNO_2 + NO \quad . . . . . (4)$$

The equilibria (1), (2), and (4) have been extensively studied, and the equilibrium constants have been measured [1,2] or calculated [3] at various temperatures. The changes of the heat content, the free energy, and the entropy are known for each of the six reactions involved. In contrast, little is known about equilibrium (3) and about the thermodynamic properties of nitrous acid vapour, although the reactions (3), (-3) have been used to prepare nitrous acid vapour for spectroscopic studies [4-6] of the molecule. A value for K_3 at 25° was determined experimentally by Wayne and Yost,[7] and was shown by them to be in fair agreement with thermodynamic data on the free energy of formation of nitrous acid in solution. They also showed that the equilibrium is established rapidly at that temperature. The entropy of HNO_2 vapour at 25° was calculated by Jones, Badger, and Moore,[6] the appropriate partition functions being calculated from the molecular constants derived from their infrared spectroscopic studies; their value was later revised.[8] The heat and the free energy of formation of HNO_2 vapour have not previously been measured.

It appeared from Wayne and Yost's data that the equilibrium constant K_3 could be determined accurately at various temperatures about 20° by combining pressure measurements with photometric measurements of the amount of nitrogen dioxide present in suitable mixtures of nitric oxide, nitrogen dioxide, and water vapour. From these values of K_3 the change of heat content and free energy of reaction (3) could be determined, and hence the thermodyanamic properties of nitrous acid vapour evaluated. It was generally possible to choose temperatures and mixture proportions with excess of nitric oxide such that the equilibria (1), (2), and (4) lay well to the left, thus keeping small the corrections for the amounts of dinitrogen trioxide and tetroxide and nitric acid present, with reasonable yields of nitrous acid.

[1] Verhoek and Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250; Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.
[2] Beattie and Bell, *J.*, 1957, 1681.
[3] Forsythe and Giauque, *J. Amer. Chem. Soc.*, 1942, **64**, 48.
[4] Porter, *J. Chem. Phys.*, 1951, **19**, 1278.
[5] D'Or and Tarte, *Bull. Soc. roy. Sci. Liége*, 1951, 478.
[6] Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **19**, 1599.
[7] Wayne and Yost, *J. Chem. Phys.*, 1951, **19**, 41.
[8] Altshuller, *J. Phys. Chem.*, 1957, **61**, 251.

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Experimental

Apparatus.—A conventional vacuum-apparatus was used for preparing, storing, and mixing the reactants. The reaction vessel was cylindrical, 20 cm. long and of 3·4 cm. internal diameter, with plane end-windows and a capillary entry tube which entered radially, opposite the mid-point of the axis. The vessel was kept in a water thermostat, and the temperature was controlled to $\pm 0{\cdot}05°$ by a Techne Tempunit and read from a calibrated mercury thermometer. Tightly fitting lengths of pressure tubing were placed between the end-windows of the reaction vessel and the windows of the thermostat to prevent the circulating water from disturbing the light used for photometry. The mixing vessel was kept in a thermostat at 73°, and the intermediate connecting tubing was heated electrically to about 80°.

Pressures were measured with a Bourdon gauge to 50 mm. Hg and on a mercury manometer above this pressure. The manometer was previously filled with nitric oxide to near the correct pressure if the mixture involved a corrosive gas. The double-beam photometric system used to measure the concentration of nitrogen dioxide was similar to that developed by Ashmore *et al.*[9] An Ilford 602 filter was used, passing wavelengths between 4500 and 5000 Å.

Nitric oxide was prepared from sodium nitrite solution and dilute sulphuric acid. The initial sample was fractionated, and the product distilled several times through a trap at −119°, and over phosphoric oxide. Nitrogen dioxide was prepared from nitric oxide and oxygen. De-aerated, distilled water was used.

Procedure.—The mixtures were prepared by two different procedures. In the first, nitrogen dioxide was measured into the reaction vessel, and a mixture of chosen pressures of nitric oxide and water vapour was prepared in the mixing vessel. This mixture was left for 20 min. to attain a uniform composition, and then admitted to the reaction vessel. The total pressure in the reaction vessel was measured when no further change occurred in the photometer reading. After 10—30 min., the reaction vessel was evacuated. Nitrogen dioxide was then admitted until the photometer signal equalled that before evacuation, and its pressure was measured. This method of determining the amount of nitrogen dioxide in the equilibrium mixture eliminated any error due to drift of the photometer over the period of mixing. It assumes that absorption of light by any other species can be neglected; this point is discussed later.

In the second method, water vapour was measured into the reaction vessel, and a mixture of nitric oxide and nitrogen dioxide was run in from the mixing vessel. The measurements were made in the same way as in the first method.

A check was made upon the time required for the mixtures to become homogeneous by diffusion by adding a large pressure of oxygen to nitrogen dioxide in the reaction vessel. The concentration of nitrogen dioxide in the end section of the vessel was followed photometrically, with the light beam directed along a diameter of the vessel. It was found that the concentration of nitrogen dioxide could rise to over three times its initial value as the oxygen was admitted, and then fell slowly until after 5 min. the increase in concentration over the initial value was less than 2%. On this basis, a minimum time of 10 min. was allowed for mixing.

Discussion

When the nitric oxide plus water mixtures, containing a mole fraction x of water, were added to nitrogen dioxide in the reaction vessel, the measured quantities were the initial and final pressures P'_{NO_2} and P_{NO_2} of nitrogen dioxide, and the total pressure at equilibrium, P_T. Then, considering the pressures, and the molar balance of NO, NO_2, and H_2O and the equilibria (1) and (2), we have

$$P_T = P_{NO} + P_{NO_2} + P_{N_2O_3} + P_{N_2O_4} + P_{HNO_2} + P_{HNO_3} + P_{H_2O}$$

$$P'_{NO_2} + 2P'_{N_2O_4} = P_{NO_2} + 2P_{N_2O_4} + \tfrac{1}{2}P_{HNO_2} + \tfrac{3}{2}P_{HNO_3} + P_{N_2O_3}$$

$$(1-x)[P_{H_2O} + \tfrac{1}{2}P_{HNO_2} + \tfrac{1}{2}P_{HNO_3}] = x[P_{NO} + P_{N_2O_3} + \tfrac{1}{2}P_{HNO_2} - \tfrac{1}{2}P_{HNO_3}]$$

$$P'_{N_2O_4} = K_1(P'_{NO_2})^2 \qquad P_{N_2O_4} = K_1(P_{NO_2})^2 \qquad P_{N_2O_3} = K_2P_{NO}P_{NO_2}$$

[9] Ashmore, Levitt, and Thrush, *Trans. Faraday Soc.*, 1956, **52**, 830; Ashmore and Levitt, Seventh Symposium on Combustion, 1959, Butterworths, London, p. 45.

Except where previously defined, the symbol P refers to the partial pressure in the equilibrium mixture. In evaluating P_{NO}, P_{H_2O}, and P_{HNO_3} from these equations, it is convenient first to evaluate approximate values by neglecting the small quantity, P_{HNO_2}, and then to calculate P_{HNO_2} from these approximate values and the equilibrium constant, K_4. The value of P_{HNO_2} can be used to obtain better values for the quantities required, and so on. Experiments at 40° and 80° with water and nitrogen dioxide only had shown that the nitric acid estimated to be formed from a nitrogen balance corresponded closely to that expected if the equilibrium (4) were attained, the equilibrium constant being based on the data of Forsythe and Giauque.[3]

With the second method of preparing the mixtures, a similar set of equations were developed. In solving these, an estimated value of P_{HNO_2} was substituted, giving pressures of the remaining components, which in turn permitted the calculation of a more accurate value of P_{HNO_2}. The values obtained by repetition of this process rapidly converged. To obtain the correct value for the mole fraction x' of nitrogen dioxide in the mixing vessel, it was necessary to allow for the small amounts of N_2O_3 and N_2O_4 also present in the mixture.

In all experiments, the addition of the mixture from the mixing vessel swept into the reaction vessel that portion of the component measured into the reaction vessel which lay in the dead space (about 1% of the total). It was shown that very little of this material diffused back into the dead space, and it was counted as part of the reaction vessel gases.

Examples of composition of equilibrium mixtures.

Expt.	Temp.	P_{NO_2} (mm.)	$P_{N_2O_4}$ (mm.)	$P_{N_2O_3}$ (mm.)	P_{NO} (mm.)	P_{H_2O} (mm.)	P_{HNO_3} (mm.)	P_{HNO_2} (mm.)	K_3 (atm.$^{-1}$)
B7	19·95°	15·50	3·40	8·00	510·5	12·90	13·70	0·041	1·40
D13 ...	80·7	17·70	0·05	0·44	440·8	98·9	10·65	0·039	0·112

There are several other possible sources of error for which it is not possible to make any satisfactory correction.

(*a*) It has been assumed that no species other than NO_2 absorbs light in the wave band used in the photometer. The spectra of gaseous NO, N_2O_4, and HNO_3 are sufficiently well known to reject them as possible absorbers, but there are no data for N_2O_3 in the gas phase. Recent work [10] with solutions of N_2O_3 showed a strong absorption in the ultraviolet region, with a weaker band ($\varepsilon \approx 20$) in the red region. At 4700 Å there is an absorption minimum, with $\varepsilon = 1$. By comparing the absorption spectra of NO_2–N_2O_4 with that of a mixture of NO, NO_2, N_2O_3, and N_2O_4, it was shown that the same general features appear in the gas phase. There is a weak absorption ($\varepsilon \approx 5$) at 7500—8000 Å, and a strong ultraviolet absorption ($\varepsilon > 170$ at 3000 Å) attributed to N_2O_3. However, at 4500—5000 Å, the difference in optical density between the mixtures was less than the possible difference due to errors in measuring the NO_2 pressure. Comparison of the absorption by N_2O_3 in solution and in the gas phase suggests that it is unlikely that $\varepsilon > 1$ for gaseous N_2O_3 at 4700 Å. If ε is taken as 1, then at 20° the value of P_{NO_2} taken for the equilibrium mixture would exceed the correct value by 0·5%, which would result in the reported value of K_3 being about 5% too low. At 40°, the error in K_3 would be 1·4%, falling further at higher temperatures. Owing to the uncertainty of the value of the extinction coefficient, however, no correction was applied.

The absorption of nitrous acid vapour has been observed [4] between 3100 and 3900 Å, and it would not be expected that the system observed could extend to 4700 Å. If nitrous acid absorbed in the photometer region, the quoted results for K_3 would be lower than the true value. The effect would be of a similar magnitude at all temperatures, as the ranges of P_{NO_2} and P_{HNO_2} used did not vary greatly with temperature.

(*b*) The pressure of water vapour used was sometimes close to the saturation value,

[10] Mason, *J.*, 1959, 1288.

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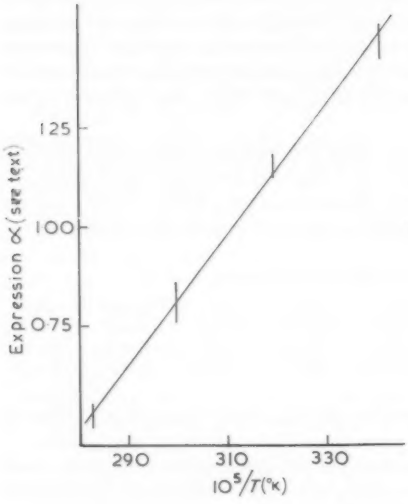
especially at 20°. It is possible that multilayer adsorption of water on the walls can remove a substantial amount from the gas phase, and act as a further source of water when some reacts to give the acids. The result of adsorption would be to make the values of K_3 too high when water was placed in the reaction vessel, and too low when it was in the mixing vessel. No correction can be applied, but the errors are reduced by taking the mean of values obtained by the two methods.

(*c*) There is some uncertainty in the correct value to take for K_2. Beattie and Bell [2] showed that the values change systematically with the pressure of NO_2 present, increasing as the pressure rises. It is not certain whether the values also change with the pressure of



The relation between α (see text) and the reciprocal of the absolute temperature.

NO, other things being equal. The value of K_2 used at 20°, the result of a direct determination in the apparatus used here, was about 6% higher than the value determined by Beattie and Bell for corresponding pressures. The error would not be important at the temperatures higher than 20°.

It is clear that these uncertain errors are only likely to affect the value of K_3 at the lower temperatures. Accordingly, the mean value of K_3 at 20° was given a weight of one-half, compared with the mean values at the higher temperatures, in determining the heat of the reaction.

Results.—The mean values of the equilibrium constant K_3 obtained by each method at the various temperatures, together with the standard deviation of the mean, σ, and the number of experiments on which the results are based are given in the following Table.

	NO and NO_2 pre-mixed			NO and H_2O pre-mixed			All expts.	
Temp.	K_3 (atm.$^{-1}$)	σ (atm.$^{-1}$)	No. of expts.	K_3 (atm.$^{-1}$)	σ (atm.$^{-1}$)	No. of expts.	K_3 (atm.$^{-1}$)	σ (atm.$^{-1}$)
19·95°	1·60	0·12	8	1·51	0·19	9	1·56	0·16
39·90	0·613	0·032	6	0·659	0·045	9	0·641	0·046
60·50	0·258	0·028	11	0·233	0·028	5	0·250	0·030
80·65	0·110	0·010	5	0·114	0·005	5	0·112	0·008

In determining the heat of reaction, allowance was made for the variation of ΔH with temperature due to the different, and varying, specific heats of reactants and

products.[8,11,12] If the difference in specific heats, $\Delta C_p°$, over the temperature range 20—80° is put in the approximate form $\Delta C_p° = a + bT$, the slope of a plot of

$$\left\{\log K_3 - \frac{a}{R}\log\frac{T}{100} - \frac{bT}{2 \times 2{\cdot}303 \times R}\right\} \equiv \{\alpha\}$$

against $1/T$ is

$$-\left\{\frac{\Delta H°_{298{\cdot}2} - 298{\cdot}2a - \frac{1}{2}b \times 298{\cdot}2^2}{2{\cdot}303\,R}\right\}$$

The results are shown plotted in this manner in the diagram. The straight line fitted by the least-mean-squares method corresponded to a heat of reaction $\Delta H°_{298{\cdot}2}$ of -9057 ± 320 cal. mole^{-1}, and an entropy change for the reaction $\Delta S°_{298{\cdot}2}$ of $-29{\cdot}89 \pm 1{\cdot}30$ e.u.

Combining these values with the heats of formation and the standard entropies [8,11] for NO, NO_2, and H_2O, we obtain the following values for nitrous acid vapour:

Standard entropy, $S°_{298{\cdot}2} = 61{\cdot}46 \pm 0{\cdot}65$ cal. mole^{-1} deg.$^{-1}$;
Standard heat of formation, $\Delta H°_{298{\cdot}2} = -18{\cdot}58 \pm 0{\cdot}20$ kcal. mole^{-1};
Standard free energy of formation, $\Delta G°_{298{\cdot}2} = -10{\cdot}81 \pm 0{\cdot}04$ kcal. mole^{-1}.

The errors quoted refer to those originating from this work only.

Both the *cis*- and the *trans*-form of nitrous acid exist in the gas phase, with an energy difference of about 500 cal., and an energy barrier of interconversion estimated [6] at 12 kcal. The entropies of each form have been calculated [8] from spectroscopic data. The entropy of mixing appropriate to the relative amounts of *cis*- and *trans*-forms at 25° being used, the spectroscopic value of the entropy of the equilibrium mixture is 60·77 e.u. The second-law value determined above is in reasonable agreement with this third-law value.

We thank Drs. J. N. Agar and B. A. Thrush for helpful discussions, and the Department of Scientific and Industrial Research for a Research Studentship (to B. J. T.).

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University of Cambridge. [*Received, September 21st*, 1960.]

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207. *The Methylation of Alkyl 3-Alkyl-2,4,6-trihydroxyphenyl Ketones and the Structure of Xanthohumol.*

By M. Vandewalle and M. Verzele.

With diazomethane 1-acetyl-2,4,6-trihydroxy-3-(3-methylbut-2-enyl)-benzene yields the 6-methoxy-, and not as stated the 4-methoxy-derivative. This can be used to prove our structure (I) for xanthohumol.

For xanthohumol, a chalcone found in hops, structure (I) was advanced [1] and confirmed [2] by us. Recently, however, Hübner and Riedl [3] proposed structure (II), their argumentation being that Robertson and Sandrock [4] proved methylation of 2,4,6-trihydroxy-1-isobutyryl-3-methylbenzene (VIII) with diazomethane to yield the 4-methoxy-derivative and that, by analogy, 1-acetyl-2,4,6-trihydroxy-3-(3-methylbut-2-enyl)benzene (III) should also give the 4-methoxy-compound (IVb). When the hydrolysis product of the substance obtained experimentally proved to be the hydrolysis product (Va) of xanthohumol they concluded that this degradation product had structure (Vb) and that the chalcone therefore

[1] Verzele, Stockx, Fontyn, and Anteunis, *Bull. Soc. chim. belges*, 1957, **66**, 452.
[2] Vandewalle and Verzele, *Bull. Soc. chim. belges*, 1959, **68**, 711.
[3] Hübner and Riedl, *Chem. Ber.*, 1960, **93**, 312.
[4] Robertson and Sandrock, *J.*, 1933, 819.

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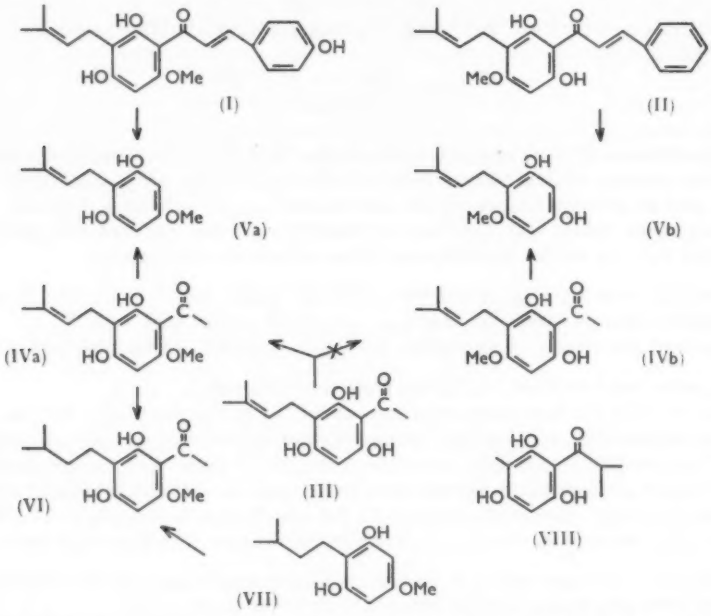
has structure (II). This particular methylation, however, produces the 6-methoxy-compound (IVa), as shown by the following facts.



Catalytic hydrogenation of the ether produces 1-acetyl-2,4-dihydroxy-3-isopentyl-6-methoxybenzene (VI) which is also obtained by a Hoesch synthesis with acetonitrile from 1,3-dihydroxy-2-isopentyl-5-methoxybenzene (VII), the identity being proved by m. p. and mixed m. p. and ultraviolet and infrared spectra. Proof of the structure of the starting material (VII) has been given earlier.[2] These facts support structure (I) for xanthohumol.

Additional proof that in this case the methylation produces the 6-methoxy-derivative comes from ultraviolet spectra. Aryl ketones with a free *p*-hydroxy-group have maximum absorption in alkaline solution at about 325 mμ, which they do not if the *p*-hydroxy-group is absent or blocked as methyl ether. This has been verified for (*a*) *p*-hydroxyacetophenone, phloracetophenone, 1-acetyl-2,4,6-trihydroxy-3-(3-methylbut-2-enyl)benzene, and the *o*-methyl ether of phloracetophenone,[5,6] and (*b*) *o*-hydroxyacetophenone, the *p*-methyl ether and the 2,4-dimethyl ether of phloracetophenone,[5,6] and 1-acetyl-2-hydroxy-4,6-dimethoxy-3-(3-methylbut-2-enyl)benzene. The monomethylation product of 1-acetyl-2,4,6-trihydroxy-3-(3-methylbut-2-enyl)benzene under discussion in this paper shows maximum absorption in an alkaline medium at 327 mμ.

There is a simple explanation for the differing methylation of phenols (III) and (VIII). The 3-methylbut-2-enyl-group in the former is large in comparison with the methyl group in the latter; and the acetyl group is small in comparison with the isobutyryl group. Orientation is therefore based on steric rather than inductive or mesomeric influences.

Experimental

1-Acetyl-2,4-dihydroxy-3-isopentyl-6-methoxybenzene (VI).—(1) On hydrogenation in presence of 5% platinum–charcoal in methanol the ether (IVa) (0·105 g.) absorbed 1 mol. of hydrogen

[5] Sonn, *Ber.*, 1928, **61**, 2300.
[6] Sonn and Bülow, *Ber.*, 1925, **58**, 1691.

in 4 min. The catalyst was filtered off and water added to produce crystallization. Recrystallized from benzene, the product (VI) (65 mg.) melted at 184—185°.

(2) Dry hydrogen chloride was passed for 30 min. through a solution of 1,3-dihydroxy-2-isopentyl-5-methoxybenzene (VII) (0·32 g.), acetonitrile (0·06 g.), and anhydrous zinc chloride (0·21 g.) in dry ether (15 ml.). The mixture was left overnight at 0°. Hydrogen chloride was again passed through the solution for 30 min. and the whole kept for 24 hr. at 0°. After removal of the ether, the imine hydrochloride was boiled for 1 hr. with water (20 ml.). *2,4-Dihydroxy-3-isopentyl-6-methoxyacetoph-one* was precipitated on cooling and, recrystallized from benzene, had m. p. 186° alone or mixed with the above product (yield, 0·17 g., 45%) (Found: C, 66·6, 67·4; H, 7·7, 7·9. $C_{14}H_{20}O_4$ requires C, 66·7; H, 7·9%).

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[*Received, October 12th*, 1960.]

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208. *The Relative Stabilities of Halogeno-complexes. Part II.*[1] *The Bond-strengths.*

By A. J. POË and M. S. VAIDYA.

The few results available for the heats of replacement of one halogen in a complex by another have been used to estimate the relative strengths of the bonds after allowance for hydration effects. Even in those complexes for which the stability order is Cl < Br < I [class (*b*)] the bond-strengths are in the order Cl > Br > I. Although for similar systems the degree of class (*b*) behaviour can be associated with a narrowing of the bond-strength differences, arguments are presented which suggest that this narrowing cannot be due to d_π-bonding effects accompanied by back-donation. Preliminary calculations, based on an ionic model, indicate that polarisation, caused by increased effective charge on the metal ion, also cannot explain class (*b*) behaviour and that ionic size may be the major factor in determining the relative bond-strengths in similar systems and thus, indirectly, the degree of class (*b*) character.

THE empirical division of metal ions into two classes, according to the relative stabilities of their complexes with certain sets of ligands, has been associated with their differing ability to form double bonds by "back-donation" of *d*-electrons to the ligands.[2] In particular, metal ions which form halogeno-complexes, the stabilities of which increase from the fluoride to the iodide, are given class (*b*) status, the iodide being assumed to be most able to attract *d*-electrons from the metal. Since this inference as to relative bond strengths is made on the basis of equilibrium constants or free energies it is of interest to derive quantitative values for these relative bond strengths.

Estimates of the relative free energies of the bonds in $[HgCl_4]^{2-}$ and $[HgI_4]^{2-}$ were made by Grinberg and Nikol'skaya[3] who considered the effects of hydration on the reaction $[HgCl_4]^{2-} + 4I^- \longrightarrow [HgI_4]^{2-} + 4Cl^-$. This calculation can be developed to obtain relative bond strengths by making use of recent data on enthalpies and entropies of formation of halogeno-complexes.[1,4] Thermodynamic functions for some halogen-interchange reactions have thus been derived and are given in Table 1. Since each equilibrium involves interchange of similar ions at a constant ionic strength the functions will be close to the corresponding standard functions. The enthalpy change for the complete interchange of halogen ligands is made up of changes in (*a*) the hydration enthalpy of the free halide ions, (*b*) the hydration enthalpy of the complex ion, and (*c*) the intrinsic enthalpy of the complex

[1] Part I, Poë and Vaidya, *J.*, 1960, 3431.
[2] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.
[3] Grinberg and Nikol'skaya, *J. Appl. Chem.* (*U.S.S.R.*), 1951, **74**, 893.
[4] Bjerrum, Schwarzenbach, and Sillén, "Stability Constants," Part II, *Chem. Soc. Spec. Publ.* No. 7, 1958, pp. 88—127.

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ion which equals minus the change in the bond strengths. By using differences in the hydration enthalpies of the free halide ions derived [5] from data quoted by Latimer [6] [*viz.*: $\Delta H°_{hydn.}$ (I^-) − $\Delta H°_{hydn.}$ (Cl^-) = 18·55 kcal./g.-ion, and $\Delta H°_{hydn.}$ (Br^-) − $\Delta H°_{hydn.}$ (Cl^-) = 8·12 kcal./g.-ion], values are obtained of the relative absolute enthalpies of the hydrated halogeno-complexes. In each of the systems considered the absolute enthalpies

TABLE 1. *Thermodynamic data for halogen-replacement reactions.*

	$-\Delta G$ (kcal./ g.-ion)	$-\Delta H$ (kcal./ g.-ion)	ΔS (cal./ deg. mole)	I (M)	ΔH (complex) (kcal./ g.-ion)
[a] $[PtCl_6]^{2-} + 6Br^- \longrightarrow [PtBr_6]^{2-} + 6Cl^-$	2·6	−4	22	0·5	52
[a] $[PtCl_6]^{2-} + 6I^- \longrightarrow [PtI_6]^{2-} + 6Cl^- \ldots$	24·6	19	19	0·5	93
[b] $[ZnCl_4]^{2-} + 4Br^- \longrightarrow [ZnBr_4]^{2-} + 4Cl^-$	−1·5	1·2	−9	4·5	31
[b] $[ZnCl_4]^{2-} + 4I^- \longrightarrow [ZnI_4]^{2-} + 4Cl^- \ldots$	−3	19·5	−75	4·5	55
[c] $[CdCl_4]^{2-} + 4Br^- \longrightarrow [CdBr_4]^{2-} + 4Cl^-$	2·6	2·6	0	4·5	30
[d] $[HgBr_4]^{2-} + 4I^- \longrightarrow [HgI_4]^{2-} + 4Br^-$	9·7	17	−24	0 (corr.)	25
$[HgCl_4]^{2-} + 4I^- \longrightarrow [HgI_4]^{2-} + 4Cl^- \ldots$	—	25 [e]	−30	0·5 [e]	49

[a] Poë and Vaidya, ref. 1. [b] Shchukarev, Lilich, and Latysheva, *Zhur. neorg. Khim.*, 1956, **1**, 225 {ΔS_2 for the formation of $[ZnCl_2]^-$ is taken as +46 cal./deg. mole, *i.e.*, as calculated from $\Delta S_2 = (\Delta H_2 - \Delta G_2)/T$, and not +63·1 cal./deg. mole as quoted in ref. 4}. [c] Shchukarev, Lilich, and Latysheva, *Uchenye Zapiski Leningrad Univ. Ser. khim. Nauk*, 1957, No. 15, 211. [d] Williams, *J. Phys. Chem.*, 1954, **58**, 121. [e] Van Eck, ref. 9(*b*), p. 98. Yatsimirskii and Astasheva, *Zhur. fiz. Khim.*, 1952, **26**, 239 (*I* variable).

of the hydrated complex ions increase from the chloride to the iodide. In order to estimate how much, if any, of this increase is due to differing bond strengths, and how much is due to the smaller hydration of the larger ion, the relative enthalpies of hydration of the complex ions must be estimated.

The Free Energies, and Enthalpies, of Hydration of the Complex Ions.—The free energies of hydration of large, weakly polarising, ions can be estimated by using the Born equation [7] which, for water at 25°, is: $\Delta G_{hydn.} = -162\ z^2/r$ kcal./g.-ion,[8] where r is the effective radius (in Å) of the ion in solution, and z is its valency. The effective radius is usually taken to be larger than the crystallographic radius by an amount which has been estimated in various ways in an attempt to obtain good agreement with measured values.[8,9] We have taken r to be equal to the metal–ligand bond length plus the van der Waals radius of the ligand, which gives an upper limit to the free-energy difference in so far as variation with radius is concerned. As an illustration of the procedure, the hexahalogenoplatinates will be considered in detail.

The Pt(IV)–Cl and Pt(IV)–Br bond lengths [10] are both close to the sums of the respective covalent radii, and an estimate of 2·54 Å can therefore be made for the Pt(IV)–I bond length. The radii of the chloro-, bromo-, and iodo-platinates are therefore taken as 4·13, 4·39, and 4·79 Å, respectively, and the hydration free energies of the hexbromo- and hexaiodo-platinate ions are then calculated to be larger (*i.e.*, less negative) than that of the hexachloroplatinate ion by 9 and 22 kcal./g.-ion, respectively.

For hypothetical, simple ions of the same charge and size as these complex ions, the entropy differences caused by differing hydration could be estimated [11] from the Born equation, or from empirical relations such as that suggested by Powell and Latimer.[12] Neither of these methods predicts entropy differences of more than a few units whereas

[5] Benjamin and Gold, *Trans. Faraday Soc.*, 1954, **50**, 797.
[6] Latimer, "Oxidation Potentials," Prentice-Hall, New York, 2nd edn., 1952.
[7] Born, *Z. Physik*, 1920, **1**, 45.
[8] Laidler and Pegis, *Proc. Roy. Soc.*, 1957, *A*, **241**, 80.
[9] (*a*) Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108; (*b*) Van Eck, "Hydration and Complex Formation of Ions in Solution," Thesis, Leiden University, 1958.
[10] Sutton *et al.*, "Interatomic Distances," *Chem. Soc. Spec. Publ.* No. 11, 1958.
[11] Cf., *e.g.*, ref. 8.
[12] Powell and Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

equilibria studies show that the partial molal entropies of the aqueous bromo- and iodo-platinate ions are larger by 60 and 97 cal./deg. mole, respectively,[1] than that of the chloroplatinate. (These differences are much larger than the 4 and 10 cal./deg. mole predicted on the basis of Cobble's empirical relation [13] between the partial molal entropies of complex ions.) Although part of the large entropy differences may be caused by different " structure-breaking " effects of these large, weakly polarising anions,[14] a large part must be due to different intrinsic entropies. Latimer (ref. 6, p. 364) has given a method for calculating intrinsic entropies of complex ions and by using his data the intrinsic entropies of the bromo- and iodo-platinate ions are estimated to exceed that of the chloroplatinate by 17 and 33 cal./deg. mole respectively. The estimated differences in the standard entropies of the aqueous complex ions, obtained by adding the solvation and the intrinsic-entropy estimates, are therefore smaller than the total entropy differences observed, and the use of such estimates in a calculation of the enthalpy changes from equilibrium-constant measurements at a single temperature would have led to large errors. *E.g.*, the complete replacement of chloride, in the chloroplatinate, by bromide would have been predicted to be exothermic by about 9 kcal./mole whereas it is, in fact, slightly endothermic (Table 1). Which of the contributions to the estimated entropy differences is likely to be more in error is not certain, but the non-spherical nature of the ions and the differing charge distributions within them will make hydration-entropy estimates very approximate. The hydration-entropy differences between the bromo- and the iodo-platinate ion and the chloroplatinate ion can therefore be taken as 22 ± 22 and 32 ± 32 cal./deg. mole, respectively, thereby allowing for the errors' arising entirely either from the hydration or from the intrinsic-entropy estimates, the former being more probable.

If the free-energy and the entropy estimates are combined, the hydration enthalpy of the bromo- and iodo-platinates are found to be larger than that of the chloroplatinate by 16 ± 7 and 32 ± 10 kcal./g.-ion, respectively, where the uncertainties are those arising from the entropy estimates. The intrinsic enthalpy of the iodoplatinate is, therefore, about 60 kcal./g.-ion larger than that of the chloroplatinate, and the average strength of the individual Pt–I bond is about 10 kcal./mole *less* than that of the Pt–Cl bond. The Pt–Br bond is calculated, in a similar way, to be about 6 kcal./mole weaker than the Pt–Cl bond. Apart from the effect of relatively small errors in the measured quantities, the uncertainties in the relative bond strengths are made up of uncertainties in the differences between the hydration enthalpies of the free halides and one-sixth of any uncertainty in the differences between the hydration enthalpies of the complex ions. Recent values of the differences for the free halides range from 16 to 24 kcal./g.-ion for the chloride–iodide difference, and from 7 to 11 kcal./g.-ion for the chloride–bromide difference.[15] (The lower values were obtained by combining free energy values, given in ref. 15*a*, with hydration entropy values derived from data in ref. 6.) The estimates of the hydration entropies of the complex ions lead to uncertainties of 1—1·5 kcal./mole in the relative bond strengths, but the uncertainties in the corresponding differences in the hydration free energies are difficult to estimate. However, calculations of the hydration free energies, based on the Born equation, are found to be more reliable than those of the entropies.[8] This would be expected on general grounds since any errors in the entropies and enthalpies caused by crudities in the model would tend to cancel each other, so that the free energy is less in error. The Born equation estimates only the electrostatic free energy, but the non-electrostatic contribution is small [8,16] and can be neglected when calculating differences.

The values for the relative bond strengths are therefore only approximate but, even if

[13] Cobble, *J. Chem. Phys.*, 1953, **21**, 1451.
[14] Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.
[15] (*a*) Randles, *Trans. Faraday Soc.*, 1956, **52**, 1573; (*b*) Brewer, Bromley, Gilles, and Lofgren, " Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., New York, 1950.
[16] Latimer, *J. Chem. Phys.*, 1955, **23**, 90.

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all the uncertainties were combined in the same sense, the order of bond strengths would not be reversed. Comparison of values for similar systems should be more accurate since the uncertainties in the hydration of the free halides, for example, will have the same effect in each system. Older enthalpy data for the halogenoplatinates [6] can be used in a similar

TABLE 2. *Relative strengths of the* M–Hal *bonds in some halogeno-complexes.*

Complex		$[PtHal_6]^{2-}$	$[ZnHal_4]^{2-}$	$[CdHal_4]^{2-}$	$[HgHal_4]^{2-}$
Bond-strength difference	M–Cl – M–Br	6	4	4·5	4
	M–Cl – M–I.....	10	9	—	7

way. The calculated strengths of the bonds again decrease from chloride to iodide but not quite so sharply.

Similar calculations have been made for the other systems given in Table 1 and the bond-strength differences are shown in Table 2. Values for the bond-lengths were obtained either from ref. 10 or by summing the covalent radii.

Although the zinc and mercury complexes were studied at very different ionic strengths a rough calculation of the relative strengths of the bonds in corresponding complexes can be made by using enthalpy changes for the reaction: $[ZnHal_4]^{2-} + Hg^{2+} \longrightarrow [HgHal_4]^{2-} + Zn^{2+}$, derived from data in ref. 4. When Hal = Cl, $\Delta H = -15$ kcal./g.-ion and when Hal = I, $\Delta H = -25$ kcal./g.-ion. Since the hydration enthalpy of Zn^{2+} is 44 kcal./g.-ion less [6] than that of Hg^{2+} the Zn–Cl bond can be shown to be slightly stronger than the Hg–Cl bond and the Zn–I and Hg–I bonds are of about the same strength.

Discussion.—Some of the estimates of relative bond strengths are supported by values of force constants derived from Raman spectra.[17] Those for the symmetrical stretching vibrations in the $[HgHal_4]^{2-}$ and $[ZnHal_4]^{2-}$ ions decrease from the chloro- to the iodo-complexes and that for $[CdI_4]^{2-}$ is less than that for $[CdBr_4]^{2-}$. The Hg–Cl force constant is less than that for Zn–Cl, and the Hg–I and Zn–I force constants are equal.

The examples considered above include some which involve metals of pronounced class (*b*) character and provide confirmation of Basolo and Pearson's conclusion [18] (based on dissociation energies of metal halides) that in all halogeno-complexes the bond strengths are in the order M–Cl > M–Br > M–I, irrespective of the order of stability constants.

Ahrland, Chatt, and Davies [2] have emphasised that any inferences as to class (*a*) or class (*b*) character must be made on the basis of heats rather than free energies. If this is applied to the $[ZnHal_4]^{2-}$ complexes it is found that zinc is a class (*b*) metal, in contrast to its previous classification.[2] The relative instability of $[ZnI_4]^{2-}$ arises because the favourable heat of formation is overcome by an unusually large and unfavourable entropy of formation.[4] Other cases of such a reversal are apparent from data in ref. 4, *e.g.*, ΔH for the reaction, $[FeCl]^{2+} + Br^- \longrightarrow [FeBr]^{2+} + Cl^-$, is $-2{\cdot}4$ kcal./g.-ion, whereas ΔG is $+1{\cdot}2$ kcal./g.-ion.

However, for halogeno-complexes, if an estimate of relative bond strengths is to be made from equilibria data, not only must the relative heats of formation be considered but quantitative allowance must also be made for solvation effects, as has been done above. The overall heat of replacement of chloride, in a complex, by iodide is determined by the relative magnitude of the opposing effects of solvation and bond strengths. In aqueous solution the bond-strength effect usually just overcomes the preferential hydration of the smaller halide ion and the chloro-complex is stronger than the iodo-complex, but when the bonding in the iodo-complex becomes relatively less weak, hydration effects become dominant, and the iodo-complex becomes the stronger. The effect of hydration of the complex ions (which favours the smaller chloro-complex) will, of course, be greater the larger the ion charge and for negatively charged halogeno-complexes the lower the oxidation state of the metal the less will solvation favour the iodo-complex. This effect might be

[17] Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.
[18] Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley and Sons, New York, 1958, pp. 179—180.

large enough to result in different stability orders for $[MHal_6]^{2-}$ and $[MHal_6]^{3-}$ and is to be contrasted with the prediction [2] that lower oxidation states of transition metals will show more class (*b*) character because of easier back-donation. The point at which the solvation–bond-strength balance changes is clearly solvent-dependent, and the borderline between classes (*a*) and (*b*) will only fortuitously be the same when defined by stabilities of halogeno-complexes, as when defined by the stabilities of complexes involving the weakly solvated uncharged ligand molecules which contain elements from groups 5 and 6. However, other things being equal, the greater the class (*b*) character the less will the difference between the M–I and M–Cl bond strength be, but this does not mean that the *absolute* strengths of the M–Hal bonds are greater—the reverse may well be true. Thus the greater class (*b*) character of Hg(II) than of Zn(II) arises partly because the Hg–Cl bond is weaker than the Zn–Cl bond while the Hg–I and the Zn–I bond are of the same strength. The much greater stability of the Hg(II) complexes is due to the relatively low heat of hydration of the Hg^{2+} ion. Although the larger size of the Hg^{2+} ion accounts for the weakness of the more ionic bonds in the hydrates, the bonding in the halogeno-complexes is more covalent owing to the larger polarisability of the halides. The covalent bonding is stronger with mercury than with zinc because of the larger ionisation potential for mercury and this just compensates for the weaker ionic bonding.

The increasing relative stability of iodo-complexes with increasing class (*b*) character has been assumed to be due to increasing covalency, and an increase in the relative strength of the M–I bond, caused either by d_π-bonding involving electron-withdrawal from the metal [2] or by increasing polarisation involving movement of electrons towards the metal.[19] Thus the stabilities of the [AgHal] complexes increase much more rapidly from the chloride to the iodide than do those of the $[CdHal]^+$ complexes, and this has been taken to reflect the greater ease of withdrawing *d*-electrons from the, formally, singly charged Ag(I) species than from the doubly charged Cd(II).[20] However, as was shown above, the larger the charge on the complex ion the more unfavourable to the iodo-complex are the solvation effects. Application of the Born equation suggests that this factor would make the increase in stability from $[CdCl]^+$ to $[CdI]^+$ about 4—5 kcal./g.-ion less than that from [AgCl] to [AgI]. The decrease in bond strength is also likely to be larger for the cadmium than for the silver complexes. This is because, first, the absolute strengths of the Ag–Hal bonds are about one-half of those of the corresponding Cd–Hal bonds. This can be confirmed by a calculation involving tabulated heats of hydration of the metal and halogen ions, estimates of the heats of hydration of the aquo- and complex ions by means of the Born equation, data for the heats of formation of the complex ions,[4] and the heat of vaporisation of water. In this way the strength of the Ag–Cl bond is found to be about 130 kcal./mole and that of the Cd–Cl bond is about 240 kcal./mole. Since the absolute bond strengths are smaller in the Ag(I) complexes, the (M–Cl)–(M–I) bond-strength differences are also likely to be smaller by a similar factor. This intuitive expectation is supported by preliminary calculations [21] of relative bond strengths, in which Garrick's treatment,[22] based on an ionic model, was used. Comparison with the zinc and the mercury complexes suggests that the difference in strength between the Cd–Cl and Cd–I bonds is about 8—10 kcal./mole and the (Ag–Cl)–(Ag–I) difference will therefore be about 4—5 kcal./mole. The size of the two main factors opposing the replacement of chloride by iodide is therefore 8—10 kcal./mole larger in the cadmium complexes, and the relative values of the stability constants can therefore be satisfactorily explained without the need for postulating different d_π-bonding effects.

Leden and Chatt have shown [23] that the replacement of the water molecule in *trans*-$[C_2H_4PtCl_2,H_2O]$ is much easier by iodide than by chloride, and that the Pt(II) is therefore

[19] Williams, *Proc. Chem. Soc.*, 1960, 20.
[20] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 1403.
[21] Poë, unpublished work.
[22] Garrick, *Trans. Faraday Soc.*, 1932, **14**, 914.
[23] Leden and Chatt, *J.*, 1955, 2936.

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acting as a strongly class (*b*) ion. However, it is generally accepted that the bond between the ethylene molecule and the platinum involves a large amount of π-bonding by back-donation of electrons from *d*- or *dp*-hybrid orbitals. This should drastically reduce any tendency to back-donation to atoms in the position *trans* to the ethylene, and the halogeno-complexes should therefore exhibit class (*a*), or weak class (*b*), behaviour if π-bonding is the decisive factor. A similar competition for *d*-electrons by ligands has been used to explain the greater stability of *cis*- than of *trans*-$[Pt(PEt_3)_2Cl_2]$,[24] and the *cis*-dihalogeno-complexes of this type should also show class (*a*) character if d_π-bonding is important. π-Bonding by back-donation does not, therefore, appear to play a significant part in determining the degree of class (*b*) character of halogeno-complexes.

The alternative explanation, whereby class (*b*) character is caused by the high polarising power of the metal ions associated with high ionisation potentials, can be tested by the calculations[21] based on the ionic model. These show that the difference in strength between the M–Cl and M–I bonds (*a*) decreases sharply with increase in the metal ion radius,† (*b*) increases with z^*, the effective charge on the metal ion, and (*c*) decreases with a decrease in the (M–Cl)–(M–I) bond-length difference such as would occur when the M–I bond becomes relatively more covalent. Thus, for tetrahedral $[MHal_4]^{2-}$ complexes, an increase in the metal ion radius from 0·8 to 1·2 Å decreases the difference by about 3 kcal./mole. When the metal ion radius is 1 Å, an increase of z^* from 2 to 2·4 increases the difference by about 3·5 kcal./mole and a decrease in the bond-length difference of 0·05 Å decreases the bond-strength difference by about 2·5 kcal./mole. These changes are large enough to account completely for reversals of stability orders. Since covalent halides also show a lessening of the (X–Cl)–(X–I) bond-strength difference as X increases in size[25] the contribution of covalency to the bonding is unlikely to modify the position appreciably.

Thus an increase in the effective charge, and polarising power, of the metal ion tends, first, to increase the difference in the bond strengths and therefore to *decrease* the class (*b*) character. This is because of the sharp increase in the absolute strengths of the bonds. This is offset by any narrowing of the bond-length difference which might occur simultaneously, and the calculated resultant of these conflicting effects probably does not have much exact significance although the effects will tend to cancel. Thus it seems likely that, in many halogeno-complexes, the size of the metal ion plays the decisive part in determining the relative bond strengths and thus, indirectly, the stability order, larger ions showing more class (*b*) character than smaller ones. The case of the Tl(I) and Tl(III) halides[2] is not necessarily in conflict with this conclusion since excitation of the inert pair into an *sp*-hybrid may occur to different extents with different halides. These calculations also suggest that there may be cases in which, although halogeno-complexes are too weak to be formed in aqueous solution, they would—if they were formed—have the class (*b*) stability order.

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[*Received, July 29th,* 1960.]

† Although differing Hal–Hal repulsion contributes towards this decrease, the main factor is the decrease in the (negative) gradient of the plot of bond strength against bond length as the bond length increases, a factor which operates even when only one ligand is present.

[24] Chatt and Wilkins, *J.*, 1952, 273.
[25] Cottrell, " The Strengths of Chemical Bonds," Academic Press, New York, 2nd edn., 1958.

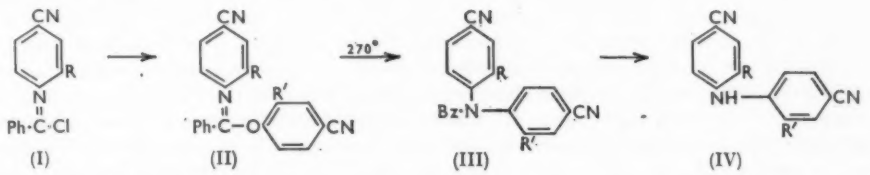
209. *The Search for Chemotherapeutic Amidines. Part XVIII.* Substituted 4,4′-Diamidinodiphenylamines.*

By A. P. T. Easson.

A series of 4,4′-diamidinodiphenylamines with substituents in the benzene rings and/or on the central amino-group is described. Most of the compounds are active against *Trypanosoma rhodesiense*, but the activity is less against *T. congolense*. The most active compound is 4,4′-diamidino-2-methoxydiphenylamine dihydrochloride with a therapeutic ratio (LD_{50}/CD_{50}) of 7·5 against the latter organism.

4,4′-Diamidinodiphenylamine,[1] one of the first aromatic diamidines to be synthesised, had only slight activity against *Trypanosoma congolense*. However, it was rather more active against *T. rhodesiense*.† Later [6] it was reported that nuclear substitution may have a marked effect on trypanocidal activity, so some substituted 4,4′-diamidinodiphenylamines have been synthesised; as a result, a few diamidines were obtained with therapeutic ratios of 4—7 against *T. congolense* but none was sufficiently active to justify further investigation.

Most of the substituted dinitriles needed for preparation of the diamidines were obtained from benzimidates by the Chapman rearrangement [7] as reported for the synthesis of the first member in this series; [1] but several modifications were introduced. Carbon tetrachloride as solvent replaced chlorobenzene in the preparation of the imidoyl chlorides (I). In the second stage the original mixture of solvents was at first used for all phenols except 4-hydroxy-3-nitrobenzonitrile whose sodium salt was insufficiently soluble in ethanol; in this instance pyridine gave satisfactory results. When pyridine was used with the other phenols or their sodium salts, the reaction time was shorter, but the yields of imidate (II) were smaller. The best results were obtained with triethylamine and the free phenols, in ether when a solvent was necessary: the reaction time was short and yields generally were much improved.



The imidates (II), with the exception of the nitro-compounds, rearranged to the benzoyldiphenylamines (III) in boiling biphenyl–diphenyl ether (cf. Chapman [7] and Wiberg and Rowland [8]). Removal of the benzoyl group to give the dicyanodiphenylamines (IV) was usually accomplished by hydrolysis with sodium hydroxide in ethylene glycol.

* Part XVII, Berg, *J.*, 1960, 5172.

† 4,4′-Diamidinodiphenylamine dihydrochloride (M & B 938) is of use in the preparation of selective media for *Haemophilus pertussis*; [2] it has also given encouraging results in the treatment of myelomatosis,[3] blastomycosis,[4] and histoplasmosis.[5]

[1] Ashley, Barber, Ewins, Newbery, and Self, *J.*, 1942, 116

[2] Lacey, *J. Gen. Microbiol.*, 1951, **5**, 6; *J. Hygiene*, 1954, **52**, 273. Nicholson and Turner, *J. Gen. Microbiol.*, 1954, **10**, 1.

[3] Ward, *Lancet*, 1958, *i*, 536; *J. Fac. Radiol.*, 1958, **9**, 221.

[4] Borelli and Rodriguez, *Trans. Roy. Soc. Trop. Med. Hyg.*, 1958, **52**, 289.

[5] Mackinnon and Stapff, *Trans. Roy. Soc. Trop. Med. Hyg.*, 1958, **52**, 290.

[6] Ashley and Harris, *J.*, 1946, 567; Berg and Newbery, *J.*, 1949, 642.

[7] Chapman, *J.*, 1925, **127**, 1992.

[8] Wiberg and Rowland, *J. Amer. Chem. Soc.*, 1955, **77**, 2205.

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2,2'-Dichloro-4,4'-dicyanodiphenylamine was prepared by chlorination of 4,4'-dicyanodiphenylamine, nitration of which gave 4,4'-dicyano-2-nitro- and thence 2-amino-4,4'-dicyano-diphenylamine. Demethylation of 4,4'-dicyano-2-methoxydiphenylamine afforded the 2-hydroxy-compound, whence alkylation yielded the other alkoxy-derivatives.

Several 4,4'-dicyanodiphenylamines containing a substituent on the central nitrogen atom were prepared. For aliphatic substituent groups, alkylation was effected with an alkyl toluene-*p*-sulphonate. *NNN'N'*-Tetra-*p*-cyanophenyl-1,3-diaminopropane was prepared by this method from 4,4'-dicyanodiphenylamine and trimethylene ditoluene-*p*-sulphonate. For aryl substituents an Ullmann reaction was carried out.

Three 4,4'-dicyanodiphenylamines with substituents in the 2- or 2,2'-positions and also on the central nitrogen atom were prepared.

4,4'-Dicyanodiphenylamine reacted only very slowly with ethyl chloroformate in presence of potassium carbonate in boiling acetone, and a pure product was not obtained. Neither 4,4'-dicyano-2-methyl- nor 4,4'-dicyano-2-methoxy-diphenylamine formed an ethoxycarbonyl derivative. Although 4,4'-dicyano-2-nitrodiphenylamine did not react with methyl toluene-*p*-sulphonate, it readily gave the *N*-ethoxycarbonyl compound when treated with ethyl chloroformate. 4,4'-Dicyano-2-hydroxydiphenylamine gave a quantitative yield of 4,4'-dicyano-*N*-ethoxycarbonyl-2-ethoxycarbonyloxydiphenylamine, but, with an excess of the dinitrile, 6-cyano-3-*p*-cyanophenylbenzoxazolone was formed, which was best prepared by semihydrolysis of the above bisethoxycarbonyl compound. This gave an intermediate monoethoxycarbonyl derivative, which suffered ring closure, even at temperatures below its m. p., with formation of the benzoxazolone.

N-Nitroso-dinitriles could not be prepared but the diamidines were readily nitrosated. 4,4'-Diamidinodiphenylamine dihydrochloride and its 2-methyl and 2-methoxy-derivatives afforded the corresponding diamidinodiphenyl-nitrosamines. These were separated from the reaction mixtures by precipitation of the bases or the sparingly soluble disulphates, and were isolated as dihydrochlorides or diacetates, all of which were stable except the dihydrochloride of 4,4'-diamidino-*N*-nitrosodiphenylamine.

Three other heterocyclic compounds derived from diphenylamine were prepared. Interaction of 2-amino-4,4'-dicyanodiphenylamine with formic acid gave 5-cyano-*p*-cyanophenylbenzimidazole. The corresponding 2-methylimidazole was made by boiling 2-acetamido-4,4'-dicyanodiphenylamine in biphenyl–diphenyl ether, whilst diazotisation of 2-amino-4,4'-dicyanodiphenylamine afforded 5-cyano-1-*p*-cyanophenylbenzo-1,2,3-triazole.

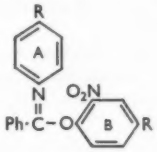
Rearrangement of the isomeric nitrobenzimidates (V and VI; R = H) was studied by Chapman.[9] The isomer (V; R = H) was smoothly converted into *N*-benzoyl-2-nitrodiphenylamine at a temperature much lower than that generally required for the reaction, but the isomer (VI; R = H) could not be rearranged. In the present work similar results were obtained when the rings A and B each contained a *p*-cyano-group; the compound (V; R = CN) was easily converted into the diphenylamine (VII) whereas the imidates (VI; R = CN) and the A,B-dinitro-analogue did not undergo rearrangement. Any explanation of the Chapman rearrangement, particularly with reference to these results with nitro-compounds, is difficult from the point of view of a mechanism involving free radicals. A mechanism which required ring closure and opening in the case of the nitro-compound (V; R = CN) would give a product isomeric with that obtained by nitration of 4,4'-dicyanodiphenylamine, whereas the same product is obtained from both reactions.

Although *N*-benzoyl-4,4'-dicyano-2-nitrodiphenylamine (VII) was readily obtained it was difficult to isolate a pure product after acid or alkaline hydrolysis. The compound was readily reduced with iron and acetic acid to 2-benzamido-4,4'-dicyanodiphenylamine (the benzoyl group must have migrated from the central nitrogen atom to the newly formed amino-group), and a pure product was not obtained after attempts to remove the benzoyl group. But 4,4'-dicyanodiphenylamine was readily nitrated and the product reduced to

[9] Chapman, *J.*, 1927, 1745.

the required 2-amino-4,4′-dicyanodiphenylamine. Benzoyl chloride in pyridine converted this into 2-benzamido-4,4′-dicyanodiphenylamine (there are no known instances of benzoylation of the diphenylamine NH group under these conditions) which was identical with the product obtained by reduction of *N*-benzoyl-4,4′-dicyano-2-nitrodiphenylamine with iron in acetic acid.

The dinitriles were usually sufficiently soluble in ethanol–chloroform and/or dioxan to afford the diethyl di-imidate dihydrochlorides smoothly, rapidly, and in theoretical



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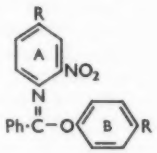

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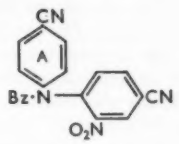

(VII)

yield when the solutions or suspensions were treated with hydrogen chloride. *NNN′N′*-Tetra-*p*-cyanophenyl-1,3-diaminopropane readily gave the tetraimidate, but tri-*p*-cyanophenylamine, owing to its sparing solubility, did not react. Two of the fusion methods [10,11] for the direct conversion of nitriles into amidines gave only very poor yields of the required triamidine, but an almost theoretical yield of tri-imidate trihydrochloride was obtained by using very finely powdered trinitrile and 2-ethoxyethanol in chloroform–dioxan. The imidate hydrochlorides were readily converted by ethanolic ammonia into the amidine hydrochlorides, which usually crystallised as hydrates. In a few cases the amidines were more readily crystallised as acetates; these were generally anhydrous.

Unsuccessful attempts were made to reduce the diamidino-nitrosamines to asymmetrical hydrazines with hydrazine [12] and with zinc and acetic acid.[13] Diphenylnitrosamine itself with zinc and acetic acid gave about 30% of diphenylhydrazine and 60% of diphenylamine.

Most of the starting materials and intermediates were prepared by standard methods, but some modifications and alternative routes are described in the Experimental section.

Experimental

4-Hydroxy-3-methylbenzonitrile [14] was first prepared from 4-hydroxy-3-methylbenzaldehyde, but was more readily made from *o*-cresol.[15]

2-Chloro-4-cyanophenol was made as described by Berg and Newbery;[6] very vigorous stirring is needed to obtain a good yield.

4-Hydroxy-3-nitrobenzonitrile [16] was obtained by nitration of *p*-hydroxybenzonitrile with a 10% solution of nitric acid in acetic acid.

N-Benzoyl-4-cyano-2-methylaniline.—This *anilide*, prepared (75%) by treatment of 4-amino-3-methylbenzonitrile [14] (obtained from 4-bromo-2-methylacetanilide by means of cuprous cyanide in pyridine) in pyridine with benzoyl chloride, had m. p. 153° (from ethanol) (Found: N, 11·6. $C_{22}H_{15}N_3O$ requires N, 11·85%) and appeared to be dimorphous; it remelted, after fusion and solidification, at 138°.

N-Benzoyl-4-cyano-2-nitroaniline, obtained similarly, had m. p. 144—146° (from ethanol).

Benzimidates.—The *N*-benzoyl-*p*-cyanoaniline (1 mol.), phosphorus pentachloride (0·98 mol.), and carbon tetrachloride (*ca.* 4 mol.) were heated under reflux. At the end of the reaction, the solvent and phosphoryl chloride were removed *in vacuo*. The residual imidoyl

[10] Oxley, Partridge, and Short, *J.*, 1948, 303; Partridge and Short, *J.*, 1947, 390.
[11] Peyron and Peyron, *Bull. Soc. chim. France*, 1953, **20**, 846.
[12] von Rothenburg, *Ber.*, 1893, **26**, 2060.
[13] Fischer, *Annalen*, 1878, **190**, 175.
[14] Paschen, *Ber.*, 1891, **24**, 3673.
[15] Ashley and MacDonald, *J.*, 1957, 1668.
[16] Auwers and Röhrig, *Ber.*, 1897, **30**, 997.

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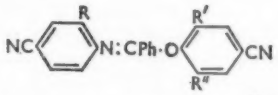
chlorides were solids (usually with low m. p.); they were readily hydrolysed by atmospheric moisture, and were not purified or characterised further. They were condensed with various *p*-hydroxybenzonitriles by one of the following processes:

(*A*) *p*-Hydroxybenzonitrile (1·1 mol.) was added to sodium ethoxide (1 mol.) in ethanol which was stirred and cooled in ice. The benzimidoyl chloride (1 mol.) in ether–chloroform was added in one portion, with stirring and cooling, followed by anhydrous sodium carbonate (0·25 mol.). The mixture was stirred at 0° for 1—2 hr. and then at room temperature for 3—4 hr. Next day the solid was filtered off and washed with water. Most of the benzimidate was usually present in this solid, but sometimes more remained in the ether–chloroform–alcohol filtrate. The products were generally recrystallised from alcohol.

(*B*) The dry sodium salt of the *p*-hydroxybenzonitrile (1 mol.) in dry pyridine was mixed with the molten benzimidoyl chloride (but the 3-nitro-chloride was first dissolved in pyridine). The mixture was heated on the steam-bath for a few min. Water was then added, and the oily precipitate which soon crystallised was filtered off and recrystallised.

(*C*) The *p*-hydroxybenzonitrile (1 mol.) and the benzimidoyl chloride were melted together. (If crystallisation occurred when the melt was cooled to about 80°, the solid was dissolved when cool, by adding a solvent, usually ether, but dioxan was used for the less soluble substances.) Anhydrous triethylamine (1·5 mol.) was then added, ether, if present, was evaporated, and the mixture refluxed for 2 hr. Water and a slight excess of acetic acid were then added and the benzimidates generally separated as oils which soon crystallised. They were usually recrystallised from alcohol and are recorded in Table 1.

TABLE 1. *Benzimidates.*



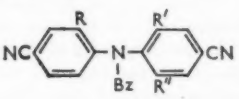
R	R′	R″	Process	Yield (%)	M. p.	Formula	Found N (%)	Reqd. N (%)
H	Me	H	A	63	142·5°	$C_{22}H_{15}N_3O$	12·25	12·5
H	Me	H	B	39	136—138	—	—	—
H	Me	H	C[a]	76	140—141	—	—	—
Me	H	H	A	45	104·5	$C_{22}H_{15}N_3O$	12·4	12·5
Me	H	H	B	—	102—104	—	—	—
Me	Me	H	A	79[b]	125—129	—	—	—
Me	Me	H	B	58[b]	123—126	—	—	—
Me	Me	H	C	83[b]	125—127	—	—	—
H	Cl	H	A[d]	25[b]	135—136	$C_{21}H_{12}ClN_3O$	11·5	11·7
Me	Cl	H	A[d]	36[b]	124	$C_{22}H_{14}ClN_3O$	11·3	11·3
H	Cl	Cl	A[d]	24[b]	167—168	$C_{21}H_{11}Cl_2N_3O$	10·8	10·7
H	NO_2	H	A[d]	47[b]	136	$C_{21}H_{12}N_4O_3$	15·1	15·2
H	NO_2	H	B	69[b]	135—136	—	—	—
H	NO_2	H	C[e]	64	134—136	—	—	—
NO_2	H	H	A	78[b]	192	$C_{21}H_{12}N_4O_3$	15·2	15·2
NO_2	NO_2	H	B	96[b]	198	$C_{21}H_{11}N_5O_5$	17·0	16·9
H	OMe	H	C	60	147—148	$C_{22}H_{15}N_3O_2$	11·95	11·9

[a] Et_2O as solvent. [b] Crude yield. [c] Product difficult to purify; the crude material was used in the Chapman rearrangement. [d] Methods B and C were not tried. [e] Dioxan as solvent. [f] The intermediate N-(*4-cyano-2-nitrophenyl*)*benzimidoyl chloride* suffered practically no decomposition when crystallised from ethanol (m. p. 142°) (Found: N, 14·9. $C_{14}H_8ClN_3O_3$ requires N, 14·7%). Ley (*Ber.*, 1898, **31**, 242) reported that *N*-(*o*-nitrophenyl)benzimidoyl chloride was less rapidly decomposed by alcohol than other imidoyl chlorides.

Rearrangement of the Benzimidates to Benzoyldiphenylamines.—Except in three cases (R = R″ = H, R′ = NO_2; R = NO_2, R′ = R″ = H; and R = R′ = NO_2, R″ = H) (Table 1), the benzimidates were dissolved in an approximately equal weight of Dowtherm (a mixture of biphenyl and diphenyl ether) and the solution was boiled for 1—2 hr. The benzoyl compounds (isolated by addition of ether) were crystallised from ethanol and are recorded in Table 2. The benzoyl derivative (R′ = R″ = H, R = Me) was not characterised but was hydrolysed directly to the corresponding diphenylamine (Table 3). One benzimidate (R = R″ = H, R′ = NO_2) rearranged smoothly in boiling anisole and even in boiling pyridine, tars being formed at higher temperatures. Two benzimidates (R = NO_2, R′ = R″ = H; R = R′ = NO_2, R″ = H) were unaffected at the lower temperatures and decomposed at 200°.

2(or 2,2′)-*Substituted* 4,4′-*Dicyanodiphenylamines* (Table 3).—Compounds 1—5 were prepared by hydrolysis of the corresponding *N*-benzoyl derivatives. A 10% solution of sodium hydroxide (1 mol.) in 75% ethylene glycol was added, in one portion, to the benzoyl compound dissolved in boiling ethylene glycol (3—4 parts). The mixture was boiled for a few min. and the product was precipitated by water and recrystallised from acetic acid.

TABLE 2. *Benzoyldiphenylamines.*



R	R′	R″	Yield (%)	M. p.	Formula	Found N (%)	Reqd. N (%)
H	Me	H	94	165—167° [a]	$C_{22}H_{18}N_2O$	12·8	12·5
Me	Me	H	98	159—160 [b]	$C_{23}H_{17}N_3O$	12·15	11·95
H	Cl	H	84	170—172	$C_{21}H_{12}ClN_3O$	11·9	11·8
Me	Cl	H	80	167—168	$C_{22}H_{14}ClN_3O$	11·6	11·3
H	Cl	Cl	54	204—205	$C_{21}H_{11}Cl_2N_3O$	10·55	10·7
H	NO_2	H	99	234—237	$C_{21}H_{12}N_4O_3$	15·4	15·2
H	OMe	H	88	152—154	$C_{22}H_{15}N_3O_2$	12·2	11·9

[a] This product was dimorphous; another form, m. p. 172·5°, was usually, but not always, obtained by crystallisation from the reaction mixture. This compound was prepared from both the isomeric benzimidates, R = R″ = H, R′ = Me, and R′ = R″ = H, R = Me, of Table 1. The rearrangement also occurred in absence of a solvent at 270°. [b] This product was dimorphous; a form with m. p. 132—133° was obtained by crystallisation from acetic acid or by solidification of the melt from the higher-melting form.

TABLE 3. *Ring-substituted* 4,4′-*dicyanodiphenylamines* (IV).

No.	R	R′	Yield (%)	M. p.	Formula	Found N (%)	Reqd. N (%)
1	Me	H	85	222°	$C_{15}H_{11}N_3$	17·9	18·0
2	Cl	H	60	211 [a]	$C_{14}H_8ClN_3$	16·25	16·6
3	Me	Me	38	199—200	$C_{16}H_{13}N_3$	16·6	17·0
4	Me	Cl	73 [b]	198	$C_{15}H_{10}ClN_3$	15·85	15·7
5	OMe	H	86	145—146	$C_{15}H_{11}N_3O$	16·85 [c]	16·9
6A [d]	NO_2	H	—	186—191	—	—	—
6B [e]	NO_2	H	95	191	$C_{14}H_8N_4O_2$	21·2	21·2
7	NH_2	H	83	238—239	$C_{14}H_{10}N_4$	23·7	23·9
8	NHAc	H	75 [f]	238—240 [f]	—	—	—
9	NHBz	H	—	233—235 [f]	$C_{21}H_{14}N_4O$ [h]	16·3	16·5
10	Cl	Cl	— [i]	243—244	$C_{14}H_7Cl_2N_3$	15·2	14·6
11	OH	H	55	257—258	$C_{14}H_9N_3O$	18·1 [c]	17·9
12	OEt	H	76	169—170	$C_{16}H_{13}N_3O$	16·3 [c]	16·0
13	OPr^n	H	73	135—136 [j]	$C_{17}H_{15}N_3O$	15·1 [c]	15·2
14	O·CH_2·CH:CH_2	H	70	135—136	$C_{17}H_{13}N_3O$	15·3 [c]	15·3
15	OBu^n	H	80	114—115	$C_{16}H_{17}N_3O$	14·6 [c]	14·4

[a] Dimorphous; resolidified melt remelted at 182°. [b] This, the best yield, was obtained by slow addition of the sodium hydroxide solution (1·15 mol.) to the benzoyl compound in boiling ethylene glycol. [c] In many instances the Dumas method gave consistently low results with diphenylamine derivatives containing an oxygen atom in the 2-position, but the Kjeldahl method was satisfactory. [d] Product formed by the Chapman rearrangement. [e] Product formed by nitration of 4,4′-dicyanodiphenylamine. Decomp. [f] By acetylation of the amino-compound (no. 7) with acetic anhydride in pyridine. [h] By reduction of *N*-benzoyl-4,4′-dicyano-2-nitrodiphenylamine (Table 2) with iron and acetic acid, or by benzoylation of the amino-compound (no. 7) in pyridine. The product was crystallised from aqueous dioxan (Found: C, 74·3; H, 4·4. Required: C, 74·5; H, 4·2%). [i] 4,4′-Dicyanodiphenylamine, partly dissolved in warm acetic acid, was treated with chlorine until a permanent excess remained. The product was crystallised successively from acetic acid, dioxan, and ethanol, but a pure sample was not obtained. [j] Mixed m. p. with no. 14 was 124—128°.

Compound no. 6A was prepared by hydrolysis of the corresponding *N*-benzoyl derivative with potassium carbonate in ethylene glycol–anisole containing a little water. The product resisted purification but an almost theoretical yield of pure nitro-compound (no. 6B) was obtained as follows: 4,4′-Dicyanodiphenylamine (40 g.) was ground with acetic acid (200 ml.), and concentrated nitric acid (400 ml.) was added. The mixture was stirred and the temperature kept below 26°. The product began to separate in *ca.* 15 min. and after a total time of 25 min. water was added, and the 4,4′-*dicyano*-2-*nitrodiphenylamine* was isolated and crystallised from anisole.

2-Amino-4,4′-dicyanodiphenylamine (Table 3, no. 7).—Reduced iron (45 g.) was gradually added to 4,4′-dicyano-2-nitrodiphenylamine (24 g.) in boiling dimethylformamide (60 ml.) and acetic acid (40 ml.). A few drops of water were added during the reduction and the mixture was heated to maintain the reaction. After 30 min. at the b. p. hot water (400 ml.) was added gradually, and the hot mixture was filtered. The solid and filtrate were worked up separately to give the amine (83%) which crystallised from anisole.

Compounds prepared from 4,4′-Dicyano-2-methoxydiphenylamine (Table 3, nos. 12—15).—Demethylation of 4,4′-dicyano-2-methoxydiphenylamine by Prey's method [17] gave the 2-hydroxy-derivative. At the required temperature (197—203°), part of the reaction mixture (1 mol. of methoxy-compound and 1·5 mol. of anhydrous pyridine hydrochloride) tended to sublime. A little Dowtherm or quinoline was added, which dissolved the sublimate, and returned it to the reaction mixture. After 4 hr. the cooled mixture was stirred with aqueous alcohol, and the solid was dissolved in a mixture of dimethylformamide and dioxan. Any methoxy-compound was precipitated by an excess of cold 5N-sodium hydroxide and acidification of the filtrate gave the 2-hydroxy-derivative (55%) which was recrystallised from acetic acid. The other 2-alkoxy-compounds were obtained by alkylation of this with the appropriate halides (ethyl and butyl iodides; propyl and allyl bromides) and potassium carbonate in boiling acetone; they were crystallised from ethanol.

Alkyl Toluene-p-sulphonates.—1,3-Trimethylene ditoluene-*p*-sulphonate (86%), m. p. 95—96°, *1,5-pentamethylene ditoluene-p-sulphonate* (85%), m. p. 80% (from ethanol) (Found: S, 15·9. $C_{19}H_{24}O_6S_2$ requires S, 15·5%), and 2-hydroxyethyl toluene-*p*-sulphonate, a syrup [*phenylurethane* (from ethanol), m. p. 135—136° (Found: N, 4·25. $C_{16}H_{17}NO_5S$ requires N, 4·2%)], were prepared by the silver salt method.[18]

Preparation of 4,4′-Dicyanodiphenylamines Substituted on the Central Nitrogen Atom (Table 4).

TABLE 4. *N-Substituted 4,4′-dicyanodiphenylamines.*

N-Subst.	Crystd. from	Yield (%)	M. p.	Formula	Found N (%)	Reqd. N (%)
Me	EtOH	89	153°	$C_{15}H_{11}N_3$ [a]	17·9	18·0
Et	EtOH	55	122—123	$C_{16}H_{13}N_3$ [b]	16·5	17·0
Pr^n	EtOH	63	96	$C_{17}H_{15}N_3$	16·0	16·1
Allyl	EtOH	71	111—112	$C_{17}H_{13}N_3$	15·9	16·2
Bu^n	Et_2O	41 [c]	80—81	$C_{18}H_{17}N_3$	15·15	15·3
n-C_8H_{13}	EtOH	60	77	$C_{20}H_{21}N_3$	13·8	13·85
$[CH_2]_3$ [d]	Dioxan	50	211—212	$C_{31}H_{32}N_6$	17·7	17·6
Ph	EtOH	78	190—191	$C_{20}H_{13}N_3$	13·9	14·25
p-NO_2·C_6H_4	Ph·NO_2	80	346	$C_{20}H_{12}N_4O_2$	16·5	16·45
p-NH_2·C_6H_4	—	73	275	— [e]	—	—
p-NC·C_6H_4	H·CO·NMe_2	57	342	$C_{21}H_{12}N_4$ [f]	17·6	17·5

[a] The alkyl group was labile and was determined by the Zeisel method (Found: "OMe," 13·3. Required: "OMe," 13·3%). [b] The alkyl group was labile (Found: "OEt," 18·0. Required: "OEt," 18·2%). [c] 1·2 mol. of K_2CO_3 used. [d] The compound is *NNN′N′*-tetra-*p*-cyanophenyl-1,3-diaminopropane. [e] The *acetyl derivative*, m. p. 206—207°, crystallised from aq.EtOH (Found: N, 15·8. $C_{22}H_{16}N_4O$ requires N, 15·9%). [f] Found: C, 78·6; H, 3·9. Required: C, 78·8; H, 3·8%.

4).—N-*Alkyl derivatives.* 4,4′-Dicyanodiphenylamine (1 mol.), with the requisite alkyl toluene-*p*-sulphonate (1·2—1·5 mol.), potassium carbonate (1 mol.), anisole, and a trace of copper bronze were boiled under reflux. The water formed in the reaction was distilled off and replaced by anisole. After the resulting solution had been refluxed for 3—4 hr. ether or chloroform was added and the mixture was filtered. The solvent was evaporated and the anisole removed *in vacuo*. The residue was washed with light petroleum (b. p. 40—60°) and recrystallised from ethanol.

N-*Aryl derivatives.* 4,4′-Dicyanodiphenylamine (1 mol.), in presence of potassium carbonate (1 mol.) and a trace of copper bronze, was treated in boiling nitrobenzene for 4—6 hr. with an excess of (*a*) iodobenzene, (*b*) *p*-bromonitrobenzene, or (*c*) *p*-bromobenzonitrile. The products from (*a*) and (*b*) were isolated by addition of chloroform and evaporation of the solvents after treatment with charcoal. The solid from (*c*) was filtered off when cold, and washed with ether, and then with water. The dried solid was extracted with hot dimethylformamide to give the product.

[17] Prey, *Ber.*, 1941, **74**, 1219.
[18] Emmons and Ferris, *J. Amer. Chem. Soc.*, 1953, **75**, 2257.

N-p-*Aminophenyl*-4,4′-*dicyanodiphenylamine*.—4,4′-Dicyano-*N*-*p*-nitrophenyldiphenylamine (1·7 g.), dissolved in boiling dimethylformamide (15 ml.) and acetic acid (2·5 ml.), was treated with reduced iron (2·5 g.) in about five portions, two drops of water being added with each. When reduction was complete the mixture was cooled and treated with water and 5N-sodium hydroxide, and the solid filtered off. Extraction with boiling dioxan, and careful addition of water to the extract, gave the amine (1·25 g.) (see Table 4).

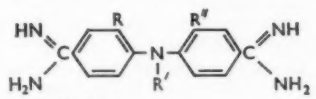
4,4′-*Dicyano*-2-*methoxy*-N-*methyldiphenylamine*.—A mixture of 4,4′-dicyano-2-methoxydiphenylamine (1 g.), methyl toluene-*p*-sulphonate (1 g.), potassium carbonate (0·8 g.), copper bronze (trace), and anisole (10 ml.) was refluxed for 3 hr. After addition of water, the anisole layer was separated, dried, and evaporated. The N-*methyl derivative* (0·95 g.), m. p. 149—150°, crystallised from ethanol (Found: N, 16·0. $C_{16}H_{13}N_3O$ requires N, 16·0%). A mixed m. p. with the starting material (m. p. 145—146°) was depressed below 135°.

4,4′-*Dicyano*-2,N-*dimethyldiphenylamine*.—This *compound*, prepared (94%) from 4,4′-dicyano-2-methyldiphenylamine and methyl toluene-*p*-sulphonate, had m. p. 112° (from ethanol) (Found: N, 16·7; NMe, 11·35. $C_{16}H_{13}N_3$ requires N, 17·0; NMe, 11·7%).

5-*Cyano*-1-p-*cyanophenylbenzimidazole*.—This *imidazole* was obtained in theoretical yield by boiling 2-amino-4,4′-dicyanodiphenylamine (5 g.) in 98—100% formic acid (25 ml.) for 1·5 hr. After crystallisation from acetic acid it had m. p. 289° (Found: N, 22·6. $C_{15}H_8N_4$ requires N, 22·95%).

5-*Cyano*-1-p-*cyanophenyl*-2-*methylbenzimidazole*.—A mixture of 2-amino-4,4′-dicyanodiphenylamine (12·5 g.), pyridine (50 ml.), and acetic anhydride (30 ml.) was boiled for 0·5 min. Addition of water gave the 2-acetamido-derivative (12·0 g.), m. p. 238—240° (decomp.), converted in boiling Dowtherm (40 ml.) in 1·5—2 hr. into the *imidazole* (8·4 g., 76%), m. p. 233° (from dioxan) (Found: N, 21·6. $C_{16}H_{10}N_4$ requires N, 21·7%).

TABLE 5. *Diamidines.*



No.	R	R′	R″	Prep. of imidate: Solvent	Time (days)	Amidine salt	Crystn. solvent	Yield (%)	M. p.
1	Me	H	H	$CHCl_3$	4	2HCl	H_2O	94	—
2	H	Me	H	,,	2	,,	Aq.EtOH & Et_2O	63	330°[a] —
3	H	Et	H	EtOH	1	,,	,,	57	>300
4	Cl	H	H	$CHCl_3$	3	,,	H_2O	38	>300
5	H	Ph	H	$CHCl_3$–dioxan	6	,,	Aq.$COMe_2$	70	>300
6	H	Bz	H	$CHCl_3$	12	,,	,,	31	280[a]
7	Me	Me	H	,,	7	,,	Aq.$COMe_2$–EtOH	47	285[a]
8	H	Bu^n	H	,,	4	Diacetate	Aq.$COMe_2$	63	275—280
9	H	Allyl	H	,,	5	,,	H_2O or Aq.$COMe_2$	67	271—273[a]
10	H	Pr^n	H	$CHCl_3$–Et_2O	1	2HCl	Aq.$COMe_2$	78	232—238
11	H	*p*-C_6H_4·C(:NH)·NH_2	H	$CHCl_3$–dioxan[g]	10	3HCl	,,	50	370—375
12	NH_2	H	H	EtOH	6	2HCl	H_2O	54	310[a]
13	H	$[CH_2]_3$[f]	H	,,	2	4HCl	Aq.$COMe_2$	67	300—310[a]
14	H	*p*-C_6H_4·NH_2	H	,,	6	Diacetate	,,	37	169[a]
15	Me	Bz	Cl	,,	1	,,	AcOH	—	225—230[a]
16	Me	H	Cl	Dioxan	2	2HCl	H_2O	70	>350
17	H	n-C_6H_{13}	H	$CHCl_3$–Et_2O	6	Diacetate	Aq.$COMe_2$	63	265[a]
18	Cl	H	Cl	,,	4	2HCl	40% EtOH	90	>350
19	Me	H	Me	Dioxan	5	,,	Aq.$COMe_2$	75	>350
20	OMe	H	H	$CHCl_3$	3	,,	,,	64	110—115[j]
21	OH	H	H	Dioxan–Et_2O	4	,,	,,	54	338—340[a]
22	OEt	H	H	$CHCl_3$	6	,,	,,	85	115—117[j]
23	OBu^n	H	H	,,	1	,,	,,	85	133—134[j]
24	OAllyl	H	H	,,	3	,,	,,	79	108—110[j]
25	OPr^n	H	H	,,	2	,,	,,	78	125—128[j]
26	H	NO	H	—	—	,,	,,	88	>300
27	OMe	Me	H	$CHCl_3$	2	Dipropionate	,,	44	193—201
28	OMe	NO	H	,,	—	Diacetate	,,	69	192—193
29	Me	NO	H	,,	—	,,	,,	93	227—228[a]

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TABLE 5. (*Continued.*)

No.	Formula	Found (%) N	Cl	Loss	Required (%) N	Cl	H_2O
1	$C_{15}H_{17}N_5,2HCl,3H_2O$	17·8	17·8	13·1	17·8	18·0	13·7
2	$C_{15}H_{17}N_5,2HCl,H_2O$	19·4	19·9	[b]	19·6	19·8	
3	$C_{16}H_{19}N_5,2HCl$	19·6	20·1	[c]	19·8	20·1	
4	$C_{14}H_{14}ClN_5,2HCl,3H_2O$	17·1	[d]	11·1	16·9		10·9
5	$C_{20}H_{19}N_5,2HCl,2H_2O$	15·9	16·2	8·35	16·0	16·2	8·25
6	$C_{21}H_{19}N_5O,2HCl,4H_2O$	13·65	14·25	15·0 [e]	13·9	14·2	14·5
7	$C_{16}H_{19}N_5,2HCl,3H_2O$	17·3			17·2		
8	$C_{18}H_{23}N_5,2C_2H_4O_2$	16·2			16·3		
9	$C_{17}H_{19}N_5,2C_2H_4O_2$	16·8			16·9		
10	$C_{17}H_{21}N_5,2HCl,2H_2O$	17·3	17·2	4·6 [f]	17·3	17·6	4·7
11	$C_{21}H_{21}N_7,3HCl,4H_2O$	17·8		12·7	17·8		13·0
12	$C_4H_{16}N_6,2HCl,3H_2O$	21·3		11·5 [h]	21·3		11·6
13	$C_{31}H_{34}N_{10},4HCl,3·25H_2O$	18·5		7·8	18·6		7·8
14	$C_{20}H_{20}N_6,2C_2H_4O_2,H_2O$	17·3		3·2	17·5		3·7
15	$C_{22}H_{20}ClN_5O,2C_2H_4O_2,1·5H_2O$	12·7		4·9	12·7		4·5
16	$C_{15}H_{16}ClN_5,2HCl,1·5H_2O$	17·5	17·9	4·2	17·4	17·7	4·5
17	$C_{20}H_{27}N_5,2C_2H_4O_2$	15·3			15·3		
18	$C_{14}H_{13}Cl_2N_5,2HCl,3H_2O$	15·35		11·5	15·6		12·0
19	$C_{16}H_{19}N_5,2HCl,H_2O$	18·6	19·2	4·8	18·8	19·1	4·85
20	$C_{15}H_{17}N_5O,2HCl,4H_2O$	16·35	16·7	16·9	16·3	16·6	16·9
21	$C_{14}H_{15}N_5O,2HCl,2·5H_2O$	17·9	18·35	4·95 [k]	18·1	18·35	4·65
22	$C_{16}H_{19}N_5O,2HCl,3H_2O$ [l]	16·9	[m]	12·2	16·6		12·7
23	$C_{18}H_{23}N_5O,2HCl,3H_2O$	15·4	15·5	12·1	15·5	15·7	11·9
24	$C_{17}H_{19}N_5O,2HCl,4H_2O$ [n]	15·2	15·8	11·5	15·4	15·65	11·9
25	$C_{17}H_{21}N_5O,2HCl,3H_2O$	15·95	16·3	11·3	16·0	16·15	11·3
26	$C_{14}H_{14}N_6O,2HCl,2H_2O$ [o]	21·5	18·3	9·1	21·5	18·2	9·2
27	$C_{16}H_{19}N_5O,2C_3H_6O_2,0·6H_2O$	15·2		2·45	15·3		2·45
28	$C_{15}H_{16}N_6O_2,2C_3H_4O_2,1·75H_2O$ [p]	18·1		6·6	18·1		6·8
29	$C_{15}H_{16}N_6O,2C_2H_4O_2,0·33H_2O$ [q]	19·8		1·4 [r]	19·9		1·4

[a] Decomp. [b] The NMe reacted in the Zeisel determination (Found: "OMe," 8·7. Required: "OMe," 9·0%). [c] The NEt reacted in the Zeisel determination (Found: "OEt," 13·5. Required: "OEt," 12·7%). [d] Found: Total Cl, 26·0. Required: total Cl, 25·8%. [e] This salt lost $2H_2O$ over H_2SO_4 *in vacuo*. [f] Only $1H_2O$ is lost. [g] 2-Ethoxyethanol was used as the alcohol in this prepn. [h] Only $2·5H_2O$ lost. [i] This compound is *NNN'N'*-tetra-*p*-amidinophenyl-1,3-diaminopropane. M. p. determined in short sealed tube. [k] Only $1H_2O$ was lost. [l] A *tetrahydrate* was also isolated, but it tended to lose water when exposed to air (Found: N, 15·4; Cl, 16·3; loss at 135°/13 mm., 16·3. $C_{16}H_{19}N_5O,2HCl,4H_2O$ requires N, 15·8; Cl, 16·3; H_2O, 16·3%). [m] Found: OEt, 10·9. Required: OEt, 10·6%. [n] Only $3H_2O$ was lost. [o] Prepared by nitrosation of 4,4'-diamidinodiphenylamine. [p] Prepared by nitrosation of 4,4'-diamidino-2-methoxydiphenylamine. [q] Prepared by nitrosation of 4,4'-diamidino-2-methyldiphenylamine. [r] At 135°/15 mm.

5-Cyano-1-p-cyanophenyl-2-phenylbenzimidazole, prepared similarly from 2-benzamido-4,4'-dicyanodiphenylamine and crystallised from ethanol, had m. p. 182° (Found: N, 17·6. $C_{21}H_{12}N_4$ requires N, 17·5%) and was dimorphous; after melting it solidified slowly and remelted at 199°.

5-Cyano-1-p-cyanophenylbenz-1,2,3 triazole.—A mixture of 2-amino-4,4'-dicyanodiphenylamine (10 g.), ethanol (100 ml.), 7·5N-isethionic acid (5 ml.), water (10 ml.), and concentrated hydrochloric acid (5 ml.) was treated, at 10°, with sodium nitrite (5 g.) in water (10 ml.) and ethanol (5 ml.). After being kept at room temperature for 3 hr. the mixture afforded the required *product* (95%), which crystallised from dioxan or acetic anhydride, m. p. 284° (Found: N, 28·0. $C_{14}H_7N_5$ requires N, 28·6%).

4,4'-Dicyano-N-ethoxycarbonyl-2-nitrophenylamine.—A mixture of 4,4'-dicyano-2-nitrodiphenylamine (1 g.), ethyl chloroformate (2 ml.), potassium carbonate (1 g.), and acetone (10 ml.) was refluxed for 2 hr. Addition of water precipitated an oil which crystallised when rubbed with light petroleum (b. p. 40—60°). The *product* (0·8 g.) separated from alcohol in pale yellow crystals, m. p. 123—124° (Found: N, 16·7. $C_{17}H_{12}N_4O_4$ requires N, 16·65%).

4,4'-Dicyano-N-ethoxycarbonyl-2-ethoxycarbonyloxydiphenylamine.—The was prepared similarly from 4,4'-dicyano-2-hydroxydiphenylamine (2 g.), ethyl chloroformate (5 ml.), potassium carbonate (2 g.), and acetone (50 ml.). The *product* crystallised from ethanol (charcoal) and had m. p. 131·5—132·5° (Found: N, 11·2. $C_{20}H_{17}N_3O_5$ requires N, 11·1%). If the reaction was carried out with an excess of dinitrile [dinitrile (2 g.), ethyl chloroformate (0·6 ml.) and acetone (30 ml.)] the product was *6-cyano-3-p-cyanophenylbenzoxazolone*, m. p. 290° (Found: N, 16·0. $C_{15}H_7N_3O_2$ requires N, 16·1%), which was prepared best as follows: A cold solution

of sodium hydroxide (1·46 g., 1 mol.) in a little water and sufficient ethanol to make 24 ml. was added gradually to the diethoxycarbonyl compound (13·8 g., 1 mol.) dissolved in cold dioxan (50 ml.) and ethanol (50 ml.). After 2—3 hr. addition of concentrated hydrochloric acid (5 ml.) and then dilution with water (700 ml.) gave an oil which quickly crystallised. The solid was boiled in Dowtherm for 5—10 min. and afforded 6-cyano-3-*p*-cyanophenylbenzoxazolone (8·8 g., 93%).

Preparation of Diamidine Salts from the Dinitriles (Table 5).—The nitriles were converted into the amidines, through the imidates, by the usual Pinner procedure. The amidines were often isolated as hydrochlorides, which were usually hydrated. Some of the more soluble hydrochlorides were not readily crystallised, and in such cases the bases were isolated and converted into the acetates which were somewhat less soluble and generally anhydrous. When heated at 95°/15 or at 135°/15 mm., or kept in an evacuated desiccator, some of the hydrochlorides lost all, and others part, of their water of crystallisation. When the salts were dehydrated to the maximum extent and then exposed to the atmosphere, all regained part, and some regained all, of the water of hydration.

4,4′-Diamidino-2-methoxy-N-nitrosodiphenylamine.—Addition of sodium nitrate (5·5 g.) in water (15 ml.) to a cold solution of 4,4′-diamidino-2-methoxydiphenylamine dihydrochloride (10·7 g.) in water (80 ml.) precipitated the sparingly soluble nitrite as a gelatinous solid. 2N-Hydrochloric acid (40 ml.) was added during 5—10 min. with cooling and stirring, and the precipitate rapidly redissolved. The solution was kept for 1 hr. 5N-Sodium hydroxide (25 ml.) was then added, and the nitrosamine base was collected and suspended in water; it became gummy. The gum was washed with water and dissolved in 20% acetic acid. Acetone was slowly added with scratching to give the crystalline diacetate (8·0 g.), m. p. 192—193° (decomp.) (see Table 5).

5-Amidino-1-p-amidinophenylbenzimidazole.—The di-imidoate was prepared in chloroform–dioxan, and the *diamidine dihydrochloride* (76%) crystallised from aqueous acetone, then having m. p. 305° (Found: N, 19·8; Cl, 16·8. $C_{15}H_{14}N_6,2HCl,4H_2O$ requires N, 19·9; Cl, 16·8%).

5-Amidino-1-p-amidinophenyl-2-methylbenzimidazole dihydrochloride (67%) (from water), m. p. 265—270° (Found: N, 20·4; H_2O, 8·5. $C_{16}H_{16}N_6,2HCl,2H_2O$ requires N, 20·4; H_2O, 8·8%), and *5-amidino-1-p-amidinophenylbenzo-1,2,3-triazole dihydrochloride* (78%) (from acetone–dilute hydrochloric acid), m. p. >350° (Found: N, 23·8; H_2O, 13·6. $C_{14}H_{13}N_7,2HCl,3H_2O$ requires N, 24·1; H_2O, 13·3%), were prepared similarly.

The author thanks Dr. H. J. Barber, F.R.I.C., and Dr. J. N. Ashley, F.R.I.C., for their interest and helpful discussions, and Mr. S. Bance, B.Sc., F.R.I.C., for the analyses.

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210. *Simple Derivatives of Cyclopentadiene. Part III.*[1] *The Adducts of Methyl Cyclopentadienecarboxylate and Cyclopentadiene.*

By DAVID PETERS.

The Diels–Alder reaction between methyl cyclopentadienecarboxylate and cyclopentadiene, known to give 60—70% of compound (II), gives also 30—40% of a second isomer. It is suggested, but not proved, that this has one of four structures (IIIa—d).

IN this and the following paper, some of the reactions of methyl cyclopentadiene-1-carboxylate (I) are reported in greater detail than before. Alder, Flock, Hausweiler, and Reiber [2] have shown that this ester with cyclopentadiene, in a typical Diels–Alder reaction, gives methyl tricyclo[5,2,1,$0^{2,6}$]deca-3,8-diene-4-carboxylate (II) in about 70% yield, the ester (I) apparently acting as dienophile. From this and other evidence, they suggested that the substituent on the cyclopentadiene ring is at position 1, as depicted in structure (I), and

[1] Part II, *J.*, 1960, 1832.
[2] Alder, Flock, Hausweiler, and Reiber, *Chem. Ber.*, 1954, **87**, 1752.

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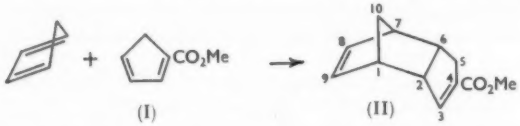
this has been supported by further evidence.[3] It is now shown that the remaining 30% of the product of reaction (I) is an isomer of (II), which, it is suggested, has one of the



(I) (II) ·····(I)

structures (IIIa—d) (a further possibility is discussed but rejected below). It is not yet possible to discriminate between these four structures, so for simplicity only formula (IIIa) is used in this discussion. In the present paper the separation of the two esters and the structure of the new ester are discussed: infrared and ultraviolet spectra are reported in the following paper.

The two esters may be separated in two ways. The first uses the difference in the rate of hydrolysis by hydroxide ion, k for (II) being 0·06 and for (III) 0·005 l. mole^{-1} min.$^{-1}$ at 50°. The German workers [2] apparently used this method but do not mention the second ester. It has been established that the new ester is a genuine product of reaction (I) and is not formed from the ester (II) during the separation. The second method is based on the addition of dimethylamine to the 8,9-double bond of the new ester to give the adduct (IV). Compound (II), in which this double bond carries no activating methoxy-

(IIIa) (IIIb) (IIIc) (IIId)

carbonyl group, is inert to the amine. The amine may be removed again from the adduct to regenerate the doubly unsaturated ester (III) in about 50% yield, simply by boiling water: no elimination occurs in acid solution, so the reaction occurs through the hydroxide. This addition of amine and its removal do not involve rearrangement. This second method is smooth and (in its first stage) complete and has proved useful also with the more complex analogues discussed in the following paper.

The structure (III) has not been established beyond doubt but is supported by the following evidence: (*a*) The dihydro-derivative (V), in which the 3,4-double bond has been saturated, forms a phenyl azide adduct. The dimethylamine adduct (IV) does not form a phenyl azide adduct. These two facts confirm the expectation that the amine adds to the reactive 8,9- and not to the 3,4-double bond. (*b*) Dimethylamine does not add to an unsubstituted 8,9-double bond, nor to the 3,4-double bond even when this carries a methoxy-carbonyl group as in (II). It is a reasonable assumption, then, that addition of dimethylamine is diagnostic of an activated 8,9-double bond. (*c*) The ultraviolet spectra

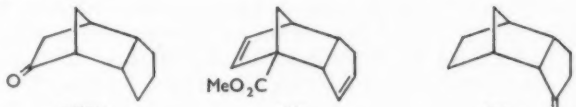
(IV) (V) (VI) (VII)

of compounds (III) and (V) are very similar, with intense maxima at 232 and 236 mμ respectively. The responsible chromophore, also present in compound (II), is often assumed to be αβ-unsaturated carboxyl group (cf. following paper). Its removal by addition of dimethylamine, as in compounds (IV) and the dimethylamine adduct of (V), removes this maximum. (*d*) The infrared spectra of compounds (III) and (V) include a

[3] Peters, *J.*, 1959, 1761.

strong band at 9·2 μ that seems to belong to the αβ-unsaturated methoxycarbonyl group (cf. following paper). When the double bond of compound (V) is removed by hydrogenation, or by addition of dimethylamine, this band moves to 9·6—9·8 μ. The infrared spectra of compounds (IV) and (V) in the 13—15 μ region are also consistent with structure (III) for the new ester.

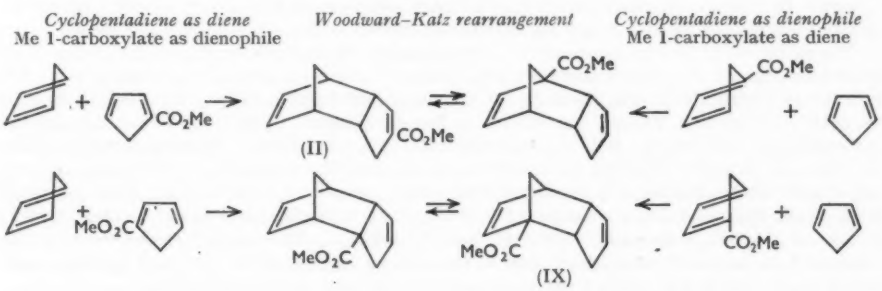
This evidence, while indicative, is not conclusive, but repeated attempts to confirm it by degradation failed. The German workers [2] degraded the acid (VI) to ketone (VII) through the azide and isocyanate. We have confirmed and improved this degradation but, despite this experience, attempts to degrade compound (V) to the known ketone (VIII) failed, apparently at or after the rearrangement of the azide stage. An alternative proof by oxidation of the double bond of compound (V) failed when this was found to give complex mixtures of acids.



(VIII) (IX) (X)

Structure (IX) (or one of its three obvious variants) has advantages over structure (III) in that it accounts for the formation (see below) of the new ester from (I), for the failure of the Curtius degradation, and for the relatively slow hydrolysis of the ester: it is, however, considered to be excluded, at least temporarily, by the evidence that the ester group is attached to a double bond.

Acceptance of structure (III) creates the problem of how it is formed from the ester (I).



(The *exo*-analogues provide a similar set.)

The problem would not arise if methyl cyclopentadienecarboxylate were a mixture of 1- and 2-isomers, but the evidence against this [3] still seems convincing and we must assume that it is a single compound, the 1-isomer. The annexed charts show all the possible

Diels–Alder reactions between cyclopentadiene and methyl cyclopentadiene-1- and -2-carboxylate, as well as the rearrangements by the Woodward–Katz mechanism.[4] They show that compound (III) cannot be formed from the 1-ester: only if a hydrogen atom shifts at some stage can structure (III) result. This shift can, in principle, occur before or during the Diels–Alder reaction.

Depolymerisation of compounds (II) and (III) has been examined: it follows the expected pattern. Compound (II) behaves very much like cyclopentadiene, in that it distils largely unchanged from a bath at 180°/100 mm. Evidently the methoxycarbonyl group on the 3,4-double bond has little or no effect on the rate of depolymerisation, as is to be expected since it is remote from the reaction centre. Compound (III), however, depolymerises almost completely under these conditions and methyl cyclopentadiene-1-carboxylate is obtained (the cyclopentadiene is lost at the low pressure used); so the ester group on [as in (III) or near as in (IX)] the 8,9-double bond accelerates depolymerisation. This is important in that it is the reason for the earlier successful syntheses of substituted cyclopentadienes.[1] Provided the dimer depolymerises at about 150°, quantitative yields of the monomers can be obtained: if a higher temperature is required, as with compound (II), the monomers repolymerise in the distilling flask and the yield of monomer is lowered.

Experimental

Spectra were recorded on a Hilger Uvispek instrument for solutions in absolute ethanol (unless otherwise specified) and on an Infracord Infrared spectrometer (1 mm. path-length, with solvent compensation) for CS_2 solutions.

Preparation of Esters.—The reaction between methyl cyclopentadiene-1-carboxylate and cyclopentadiene was carried out as described by Alder *et al.*[2] The mixed product had b. p. 76—86°/0·1 mm. (lit.,[2] 62—70°/0·05 mm.) (Found: C, 76·1; H, 7·6. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%). Comparison of the infrared spectrum of this mixture with that of an artificial mixture of the two esters indicated the presence of 35 ± 5% of the new ester.

The mixture (20 g.) was dissolved in dimethylamine (50 ml.) and kept at 0° for 16 hr. The oil which remained after removal of the excess of amine *in vacuo* was taken up in ether, extracted with dilute hydrochloric acid (from 25 ml. of concentrated acid), dried, and distilled, to give ester (II) (13·0 g.), b. p. 76—84°/0·1 mm., m. p. 39—41° (Found: C, 76·5; H, 7·7%), $\lambda_{max.}$ 228 mμ (log ε 3·88), $\nu_{max.}$ (strong) 9·1, 9·2 (conjugated CO_2R), 13·2, and 13·65 μ. The completeness of the reaction was shown by treating this material again with dimethylamine. The acidic aqueous layers were made alkaline and extracted with ether. Removal of the solvent from the dried extract gave the dimethylamine *adduct* (IV) (6·65 g.) as a colourless oil (Found: C, 71·4; H, 9·1; N, 5·8. $C_{14}H_{21}NO_2$ requires C, 71·45; H, 9·0; N, 5·95%). The ultraviolet spectrum of this compound showed only weak absorption in the 220 mμ region and the infrared spectrum had strong bands at 9·5, 9·6, and 9·7 (unconjugated CO_2Me) and at 13·5 and 14·4 μ.

The amine adduct (6·6 g.) was refluxed with water (50 ml.) for 15 min., then cooled, acidified, and extracted with ether. Removal of the solvent from the dry extract gave the new *ester* (3·1 g.), b. p. 60—62°/0·1 mm., m. p. 30—33° (Found: C, 76·1; H, 7·4%), $\lambda_{max.}$ 232 mμ (log ε 3·76), $\nu_{max.}$ (strong) 9·2 (conjugated CO_2Me), 13·0, 14·0, and 14·6 μ.

Reactions of Ester (II).—(*a*) Alkaline hydrolysis of the ester (6·7 g.) was complete in 10 min. in a 50% excess of refluxing 10% sodium hydroxide solution. The acid (5·86 g.) was precipitated on acidification and, crystallised from ethyl acetate, had m. p. 148° (lit.,[2] 148°) (Found: C, 75·2; H, 7·0%; *M*, 178. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·9%; *M*, 176), $\lambda_{max.}$ 224 mμ (log ε 3·96). Re-esterification with refluxing methanol containing sulphuric acid gave an oil whose infrared spectrum was identical with that of the starting ester.

(*b*) Hydrogenation of the acid (4·0 g.) in ethanol over platinum at room temperature and 1 atm. led to rapid uptake of 505 ml. of hydrogen ($1H_2 = 512$ ml.). Crystallisation of the product from ethyl acetate gave the dihydro-acid (VI), m. p. 152—153° (lit.,[2] 153°) (Found: C, 74·0; H, 7·9%; *M*, 177. Calc. for $C_{11}H_{14}O_2$: C, 74·1; H, 7·9%; *M*, 178), $\lambda_{max.}$ 226 mμ (log ε 3·97). A mixture of this dihydro-acid and the unsaturated acid (m. p. 148°) had m. p. 147—148°. Selective hydrogenation of the ester (II) to its dihydro-derivative (strong infrared bands at 9·2, 9·3, and 13·35 μ) followed by hydrolysis gave the same dihydro-acid.

[4] Woodward and Katz, *Tetrahedron*, 1959, **5**, 70.

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(*c*) Curtius degradation of the dihydro-acid (VI) was carried out as follows. The *acid chloride*, prepared by refluxing the acid (1·39 g.) with an excess of thionyl chloride for 30 min., was an oil (1·41 g.) (Found: C, 67·4; H, 6·8; Cl, 17·7. $C_{11}H_{13}ClO$ requires C, 67·2; H, 6·6; Cl, 18·1%), $\lambda_{max.}$ 246 mμ (log ε 4·02) in spectroscopic hexane. Reaction of the acid chloride with methanol regenerated the methyl ester, and aqueous hydrolysis regenerated the acid. The azide was prepared by shaking a solution of the acid chloride (1·37 g.) in acetone (20 ml.) with a solution of sodium azide (0·75 g.) in water (3 ml.) for 10 min.; extraction with ether then gave the azide (1·16 g.) as a white solid, $\lambda_{max.}$ 256 mμ (log ε 4·07). The azide (1·15 g.) was heated in toluene (30 ml.) to 100° for 30 min. (170 ml. of gas evolved; $1N_2 = 127$ ml.). Removal of the toluene *in vacuo* left the oily *isocyanate* (0·98 g.) (Found: C, 76·8; H, 7·6; N, 9·0. $C_{11}H_{13}NO$ requires C, 75·4; H, 7·5; N, 8·0%). The isocyanate (0·94 g.) was refluxed with concentrated hydrochloric acid (10 ml.) for 10 min.; the neutral product was a wax (0·81 g.) which was repeatedly sublimed at 10 mm. to give ketone (VII), m. p. 105—106° (lit.,[2] 115°) (Found: C, 79·3; H, 9·1. Calc. for $C_{10}H_{14}O$: C, 79·95; H, 9·4%), for which the carbonyl band is at 5·7 μ and, as the only strong band above 7·5 μ, there is a band at 8·6 μ. A mixture of ketone (VII) and ketone (X), m. p. 102—104°, had m. p. 103—105°. The semicarbazone of ketone (VII) had m. p. 205—206° (lit.,[2] 215°) after several crystallisations from ethanol (Found: C, 63·8; H, 8·3. Calc. for $C_{11}H_{17}N_3O$: C, 63·7; H, 8·3%). A mixture of this semicarbazone and the semicarbazone of ketone (X) (m. p. 196—197°) had m. p. 180—185°. The infrared spectra of ketones (VII) and (X) are distinct. Hydrolysis of the isocyanate by refluxing it with water for 30 min. gave impure ketone (VII). The infrared spectrum and the preparation of the semicarbazone showed that ketone (VII) was the main constituent of the mixture.

Reactions of the New Ester.—(*a*) Alkaline hydrolysis of the ester (0·96 g.) with a 50% excess of refluxing 10% sodium hydroxide solution required 60 min. for completion. The *acid* (0·7 g.) precipitated by acidification had m. p. 128—129° (from ethyl acetate) (Found: C, 75·4; H, 7·4%; *M*, 180), $\lambda_{max.}$ 230 mμ (log ε 3·78). Re-esterification as above gave an oil whose infrared spectrum was identical with that of the starting ester.

(*b*) A mixture of the dimethylamine adduct (IV) (0·25 g.) and phenyl azide (0·25 g.) was kept for 24 hr. at room temperature. The basic product was an oil (0·22 g.) whose infrared spectrum was identical with that of compound (IV).

(*c*) Hydrogenation of the new ester and its acid does not proceed selectively at the 8,9-double bond: both double bonds of ester (III) are hydrogenated at comparable rates. Selective hydrogenation of the 3,4-double bond is possible before the removal of the amine from the adduct (IV). Hydrogenation of the adduct (IV) (6·8 g.) in dilute hydrochloric acid over platinum at room temperature and 1 atm. led to the uptake of 665 ml. ($1H_2 = 650$ ml.). An ethereal extract of the alkaline aqueous solution gave the *dimethylamine adduct* (5·85 g.) of the dihydro-derivative as an oil (Found: C, 70·7; H, 9·8; N, 5·9. $C_{14}H_{23}NO_2$ requires C, 70·85; H, 9·8; N, 5·9%), which had no intense absorption in the ultraviolet above 210 mμ and no olefinic band in the 13—15 μ region. Removal of the dimethylamine from the adduct (5·8 g.) by boiling water in 20 min. gave the *dihydro-ester* (V) (2·5 g.), b. p. 70—72°/0·1 mm. (Found: C, 74·9; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%), $\lambda_{max.}$ 236 mμ (log ε 3·83), $\nu_{max.}$ (strong) 9·1, 9·2 (conjugated CO_2Me), and 13·05 μ. Further hydrogenation of compound (V), to the tetrahydro-stage, gave an oil whose infrared spectrum was identical with that obtained by complete hydrogenation of ester (III).

(*d*) Alkaline hydrolysis of ester (V) (1·7 g.) with refluxing sodium hydroxide solution required 60 min. for completion. Acidification gave the *acid* (1·42 g.), m. p. 121—122° (from ethyl acetate) (Found: C, 73·6; H, 7·95%). Re-esterification as above gave an oil whose infrared spectrum was identical with that of the starting ester (V).

Rates of Hydrolysis of the Two Esters.—The ester (~ 0·4 g.) was warmed in methanol (~ 15 ml.) to 50°. N-Sodium hydroxide (3 ml.) was added (time zero) and the solution immediately made up to 20 ml. with methanol. Samples (2 ml.) were withdrawn at intervals and titrated against 0·1N-hydrochloric acid (Bromothymol Blue). The second-order plots were straight lines: the velocity constants are reported in the discussion.

Depolymerisation.—(*a*) Compound (II) (2·0 g.) was distilled at 100 mm. (bath-temp. 180°, vapour-temp. 140—150°), to give a distillate (1·4 g.) whose infrared spectrum resembled that of compound (II). The intensity of the strong monomer band at 14·8 μ suggested that some 15% of monomer was present in the distillate.

(*b*) Compound (III) (1·96 g.) was distilled at 100 mm. (bath-temp. 180°, vapour-temp.

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120—125°), to give a colourless oil (0·83 g.) whose infrared spectrum (band at 14·8 μ) resembled that of the monomer (I). After spontaneous dimerisation of this product at room temperature for 24 hr., the spectrum changed to that of the mixed tricyclodecadiene esters and crystallisation from light petroleum (b. p. 40—60°) gave Thiele's ester [3] (0·37 g.), identical in m. p., mixed m. p., and infrared spectrum with an authentic sample.

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[*Received, August 5th*, 1960.]

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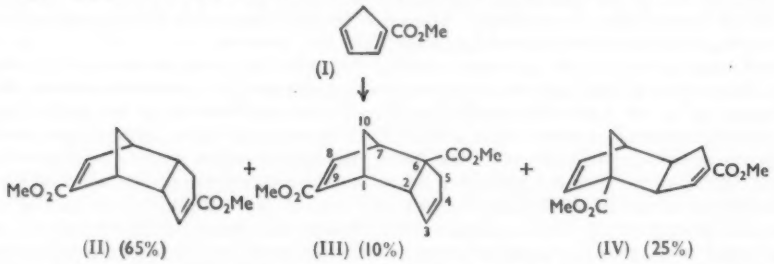
211. *Simple Derivatives of Cyclopentadiene. Part IV.*[1] *The Dimerisation of Methyl Cyclopentadiene-1-carboxylate.*

By DAVID PETERS.

Dimerisation of methyl cyclopentadiene-1-carboxylate gives three dimers, whose structures are deduced by combination of chemical and spectroscopic results. The kinetic and spectroscopic evidence does not reveal complexity in the dimerisation, although the suggested structure of the main reaction product implies that the reaction is not simple.

THE preceding study [1] of the Diels–Alder reaction between methyl cyclopentadiene-1-carboxylate and cyclopentadiene has been extended to the reaction of this ester with itself. This reaction is summarised in the scheme below.

In the absence of a solvent, methyl cyclopentadiene-1-carboxylate (I) dimerises spontaneously at room temperature, giving Thiele's ester [2] (65%), whose suggested structure is (II), a second solid dimer [3] (10%), to which is assigned a structure such as (III), and a liquid



dimer (25%), to which is assigned a structure such as (IV). There are closely related alternatives for each of the suggested structures, and it is not yet possible to discriminate between these: for example, the 6-methoxycarbonyl group in compound (III) * may be on carbon-2 or -5). The structures written here are those that require a minimum of structural reorganisation during the dimerisation.

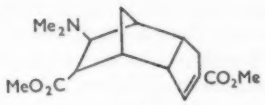
The liquid isomer is easily isolated from the mixture since it does not react with dimethylamine whereas the other two give the adducts (V) and (VI) (see ref. 1). Separation of the isomers (II, III) or (V, VI) was effected by chromatography. The parent esters are regenerated from the amine adducts (V) and (VI) by boiling water.

The structures of the three esters have been deduced by a combination of chemical and spectroscopic evidence. Our first assumption, that addition of dimethylamine is diagnostic

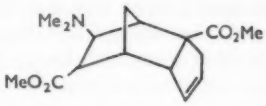
* Throughout this discussion a double bond in the isolated cyclopentene ring is designated 3,4-, the numbering which it has in the parent hydrocarbon. It may be noted that according to strict nomenclature it acquires numbers 4,5 when the ester groups are given priority for lowest numbers; this strict numbering is used in the Experimental section.

[1] Part III, preceding paper.
[2] Thiele, *Ber.*, 1901, **34**, 68; 1900, **33**, 666.
[3] Peters, *J.*, 1959, 1761.

of an activated bicycloheptene 8,9-double bond,[4] has been checked, in part, by showing that the adducts (V) and (VI) do not react with phenyl azide, as they should if they contained an 8,9-double bond. If this is correct it is possible to interpret all the other evidence in a consistent fashion.



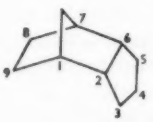
(V)



(VI)

The compounds to be considered and their relevant spectroscopic properties are listed in the Table. We assume that structures (XIII) to (XX) are known to be as shown. The first correlation is that the moderately intense (ε 100—200) infrared bands in the 9—10 μ region are associated with a complex vibration of the methoxycarbonyl group: their position then shows whether there is a double bond conjugated with this group. As shown in the fourth column of the Table there is a singlet or doublet at 9·1—9·2 μ when αβ-unsaturation is present; when there is not, then this band occurs at 9·6—9·8 μ, usually as a doublet, occasionally as a triplet. In only one case (XXIII) is there ambiguity in this interpretation.

Spectroscopic bands for derivatives of bicyclo[5,2,1,$0^{2,6}$]*decane*



No.	Unsatn.	Substituents	9—10 μ	13—15 μ	$\lambda_{max.}$ (m μ)	log ε
XIII	3,4	—	—	13·6s, 14·75m	—	—
XIV	8,9	—	—	13·7s, 14·2m, 14·5w	—	—
XV	3,4; 8,9	—	—	13·3s, 13·8s, 14·2m, 14·85m	—	—
XVI	3,4; 8,9	4-CO_2Me	9·1, 9·2	13·2s, 13·65s, 13·9w, 14·15w	228	3·88
XVII	3,4	4-CO_2Me	9·15, 9·25	13·35s, 14·2w	225	3·78
XVIII	3,4; 8,9	9-CO_2Me (D)	9·2	13·0s, 13·25w, 14·0m, 14·6m	232	3·76
XIX	8,9	9-CO_2Me (D)	9·2	13·05s, 13·7w	236	3·80
XX	3,4	9-CO_2Me, 8-NMe_2	9·5, 9·6, 9·7	13·5m, 14·4m	—	—
II	3,4; 8,9	4,9-$(CO_2Me)_2$ (D)	9·1, 9·2	13·05s, 13·7s, 14·0w	220	4·12
XXI	3,4	4,9-$(CO_2Me)_2$ (D)	9·1, 9·2; 9·6, 9·7	13·0m, 13·4s, 13·9w 13·0m, 13·3s, 14·0w	228 227	3·76 3·90
V	3,4	4,9-$(CO_2Me)_2$, 8-NMe_2	9·2; 9·6, 9·7, 9·8	13·4s, 13·8w	228	3·88
XXII	8,9	4,9-$(CO_2Me)_2$ (D)	9·2; 9·7	13·05s	234	3·82
III	3,4; 8,9	6,9-$(CO_2Me)_2$ (D)	9·2; 9·6, 9·7	13·0s, 13·2m, 13·8m, 14·4m	231	3·81
VI	3·4	6,9-$(CO_2Me)_2$, 8-NMe_2	9·6, 9·7	13·5m, 14·2m	—	—
IV	3,4; 8,9	1,4-$(CO_2Me)_2$	9·1; 9·5	13·2s, 13·6s, 14·2w	226	3·95
XXIII	3,4	1,4-$(CO_2Me)_2$	9·2, 9·3	13·4s, 14·1w	225	3·93
XXIV	3,4	4,9-$(CO_2Me)_2$, 8-MeO	9·1, 9·2; 9·7	13·35m, 13·8m	228	3·90
XXV	—	4,9-$(CO_2Me)_2$, 8-NMe_2	9·55, 9·7	—	—	—
XXVI	—	4,9-$(CO_2Me)_2$	9·6, 9·7	—	—	—
XXVII	—	9-CO_2Me	9·6, 9·7	—	—	—
XXVIII	—	9-CO_2Me, 8-NMe_2	9·6, 9·7	—	—	—

D denotes that the compound adds dimethylamine. ε values: s = >200; m = 50—200; w = <50.

The second, rather more involved, correlation concerns the olefinic out-of-plane vibrations at 13—15 μ. These bands are the most prominent in the 7·5—15 μ spectrum of the parent hydrocarbons (XIII—XV). When both the 3,4- and the 8,9-double bond are

[4] Peters, *J.*, 1960, 1832.

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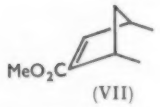
present (XV), interaction between the strong bands of almost equal frequency (13·6 and 13·7 μ) which originate in the separate double bonds of compounds (XIII) and (XIV) gives two new intense bands at 13·3 and 13·8 μ. The 14·75 μ band of (XIII) and the 14·2 μ band of (XIV) [5] survive almost unchanged in the doubly unsaturated compound (XV). Now all the compounds that add dimethylamine (marked D in the Table), but none of those compounds that do not add dimethylamine, have a strong band at 13·00—13·05 μ. Further, those that react with the amine all † show ultraviolet absorption at or above 231 mμ, while those which do not react with it absorb at or below 228 mμ. These three features together are characteristic of the partial structure (VII). The 13·00—13·05 μ band is not affected by the presence or absence of a 3,4-double bond. The compounds that (i) do not react with dimethylamine but (ii) contain an 8,9-double bond (nos. IV, XVI) have a strong band at 13·20—13·25 μ and this is associated with partial structure (VIII). A band occurs at 13·60—13·80 μ when there is an αβ-unsaturated ester group in the isolated cyclopentene ring provided that an 8,9-double bond is also present, *i.e.*, structure (IX) as in compounds (II, III, IV, XVI); when the 8,9-double bond is absent, as in compounds (V, XVII, XXI, XXIII, XXIV), this band moves to 13·30—13·40 μ, *i.e.*, structure (X). Further, any bands of medium intensity at wavelengths longer than 14·2 μ are due to an unsubstituted 3,4-double bond (cases III, XVIII, XIII, XX, VI, XV), but the exact position of this band varies from case to case.

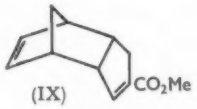
This set of correlations, based originally on the spectra of the known compounds, interprets also the spectra of the new compounds intelligibly and unambiguously. (Additional evidence relating to the structures of various compounds may be found in the Experimental section.)

Several further points about the dimers (II—IV) require mention. First, an earlier inference by the present author [3] about the ultraviolet spectrum of compound (II) must be corrected. When the 8,9-double bond of compound (II) is hydrogenated, a band at about 216 mμ disappears from the ultraviolet spectrum; but it cannot be inferred that this band is due to an *isolated* αβ-unsaturated ester group in the bicycloheptene system, because this group is now known to absorb at 231—236 mμ. Evidently there is interaction between the excited states of the two chromophores, and this is strongest when the two chromophores are identical, as in this case. When the chromophores are not identical, the inter-

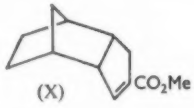


(VII)

(VIII)



(IX)



(X)

action is small, but not zero (cf. the pairs XVIII/XIX and XVI/XVII). This wrong inference led on to an incorrect structural assignment [3] for compound (III), the 103° isomer. This has the double-bond conjugation in position 8,9, not in 3,4, since it has $\lambda_{max.}$ 231 mμ, it has a strong 13·0 μ band, and *both* the 9·2 and the 9·6—9·7 μ bands of conjugated and unconjugated ester groups. Further, it adds dimethylamine with the disappearance of the ultraviolet maximum, and a medium-intensity band is present at 14·4 μ in the infrared spectrum, suggesting an unsubstituted 3,4-double bond.

The third isomer (IV) is assigned an *exo*-structure, as Weise [6] suggested, since it is a liquid. Depolymerisation of this isomer has been found to resemble that of Thiele's ester (II): heating at about 160°/10 mm. causes slow distillation of methyl cyclopentadiene-1-carboxylate, identical with the material obtained by depolymerising Thiele's ester.

† Except for (II) which has two interacting chromophores.

[5] Cristol and Lalonde, *J. Amer. Chem. Soc.*, 1959, **81**, 5417; Schmerling, Luigi, and Welsh, *ibid.*, 1956, **78**, 2819.

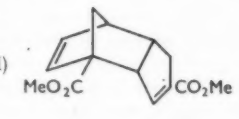
[6] Weise, U.S.P. 2,781,395, 2,716,662.

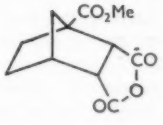
Certain of the derived compounds (XXI—XXVIII) require comment. Compound (XXI), the dihydro-derivative of Thiele's ester, exists in two forms, presumably with different configurations of the 9-ester group. Compound (XXII) is obtained by hydrogenating the dimethylamine adduct (V) of Thiele's ester and then removing the amine; it is a liquid, evidently a mixture of non-isomorphous isomers. Compound (XXIV), in which methanol has been added to the 8,9-double bond of Thiele's ester, is one of the products from the esterification of the crude dimeric cyclopentadienecarboxylic acid.[7] During alkaline hydrolysis of the ester groups the methanol is lost, so that the hydrolysis product is Thiele's acid.

When the two double bonds of dicyclopentadiene and its derivatives are hydrogenated two effects operate. The 8,9-double bond of dicyclopentadiene is more easily hydrogenated than the 3,4-double bond; and the rate of hydrogenation of both double bonds is slowed down by an attached ester group. So, in the parent hydrocarbon (XV), differential hydrogenation of the 8,9-double bond is possible. In compounds (IV) and (XVI), the two effects reinforce each other and selective hydrogenation of the 8,9-double bond is very easy. But in compound (XVIII), the effects are opposed and the rate of hydrogenation of the 8,9-double bond is slowed down so that both bonds are hydrogenated at comparable rates and selective hydrogenation bond is impossible; it is, in fact, possible to hydrogenate the 3,4-double bond of this compound, to give (XIX), by using a method mentioned in the preceding paper.

Another possible structure for Thiele's ester (II) has to be considered, namely, (XI). The situation is like that discussed in the previous paper (the structure of the " new " ester), in that the structural evidence is apparently conflicting. Structure (XI) makes the dimerisation of methyl cyclopentadiene-1-carboxylate easy to understand, but then the addition of dimethylamine and the ultraviolet spectra are very difficult to interpret. Further, if Thiele's ester had structure (XI), then the liquid isomer can hardly have structure (IV): it would presumably have to have its ester group in the 10-position, and this is not likely. Also, the maleic anhydride adduct of methyl cyclopentadienecarboxylate could not have the analogous structure (XII), since it shows no intense ultraviolet absorption above 210 mμ, and requires the ester group in the 10-position. So we retain, for the present, structure (II) for Thiele's ester and accept the consequence that dimerisation is a complex reaction.

(XI)





(XII)

Course of the Dimerisation.—The dimerisation of methyl cyclopentadiene-1-carboxylate has been carried out in the presence and absence of a solvent, at elevated temperatures, and in the presence of 100 moles % of acid. None of these modifications affects the product composition appreciably. The effect of added base (sodium methoxide in methanol) is more complicated, since it ionises the monomer (I); but in small amounts (5 moles %) it does not affect the course of the reaction markedly. It does, however, lead to the formation of a small amount of compound (XXIV) in which methanol has been added to the 8,9-double bond of Thiele's ester.

These results give no indication of the suspected complication in the reaction. Nor do the kinetics, which were followed by measuring the rate of disappearance of the monomer peak at 270 mμ. The reaction is accurately of the second order, the velocity constant being about two hundred times greater than that for cyclopentadiene dimerising under similar conditions.[8] The acceleration is due to both a lower activation energy and

[7] Ziegler, Kulhorn, and Hafner, *Chem. Ber.*, 1956, **89**, 434.
[8] Wassermann, *J.*, 1936, 1034.

XUM

(probably) an increased pre-exponential factor in the Arrhenius equation. During the dimerisation, the growth of the dimer absorption band at 220 mμ is synchronous with the disappearance of the monomer band. There is also a well-formed isobestic point at 246 mμ, showing that there is no appreciable build up of a compound having light absorption different from that of the two main components of the product mixture. This evidence then is also consistent with structure (XI), rather than structure (II), for Thiele's ester.

Experimental

For details of spectral measurements see the preceding paper. Light petroleum was the fraction of b. p. 40—60°, unless otherwise specified.

Preparation of Thiele's Ester (II).—For large-scale preparations of this compound, the method of Ziegler *et al.*[7] (pouring a decalin suspension of sodium cyclopentadienide on to solid carbon dioxide) is more convenient than the Grignard method described earlier. The product is a mixture containing about 60% of Thiele's acid. The crude acid was partly purified by one crystallisation from methanol and the purification completed after the esterification. The impurities (which have not been examined) in the crude acid were a methanol-insoluble solid acid and liquid acids. The partly purified acid was esterified by refluxing its solution in methanol containing a little sulphuric acid for 16 hr. The product was crystallised from light petroleum (b. p. 60—80°): the overall yield of Thiele's ester from sodium cyclopentadienide is about 40%. The filtrate from this crystallisation gives compound (XXIV) (cf. below).

Dimerisation of Methyl Cyclopentadiene-1-carboxylate (I).—Depolymerisation of Thiele's ester to methyl cyclopentadiene-1-carboxylate was reported earlier.[3] Reconversion into the dimer is complete in the absence of solvent in an hour at room temperature. The composition of the product mixture (10·05 g.) was determined by first crystallising it from light petroleum (b. p. 60—80°) (100 ml.), to give pure Thiele's ester (5·57 g.), and recovering the oil (3·96 g.) from the filtrate. The composition of this oil was determined by comparison of its infrared spectrum with that of artificial mixtures of Thiele's ester (II), the 103° isomer (III), and the liquid isomer (IV). The overall proportions, which varied slightly in different reactions, were Thiele's ester 65(±3)%; 103° isomer 10(±2)%; liquid isomer 25(±3)%.

Dimerisation of the cyclopentadiene ester (*ca.* 1 g.) in ethanol (20 ml.) at room temperature for 24 hr. and at the b. p. for 1 hr. gave the same product mixture as the above. Dimerisation of the monomer (*ca.* 1 g.) in methanol (10 ml.) containing concentrated hydrochloric acid (0·5 ml.) at room temperature for 3 days also gave the same product mixture. Dimerisation of the monomer (*ca.* 1 g.) in methanol (10 ml.) containing sodium methoxide (5 moles %) gave similar results, except that extra infrared peaks were present in the neutral oil obtained after removal of Thiele's ester and the 103° isomer with dimethylamine. These peaks corresponded with those expected if about 5% of compound (XXIV) was present in the original dimerisation mixture.

Separation of the Dimers.—Separation of the 103° isomer from the dimerisation product mixture has been described.[3] To separate the liquid isomer, the crude product (10·26 g.) was crystallised from light petroleum (b. p. 60—80°) to remove the bulk of the Thiele's ester (5·57 g.), and the oil (3·79 g.) was recovered from the filtrate, dissolved in dimethylamine (20 ml.), and kept at 0° for 16 hr. The neutral product from this reaction is the liquid *isomer* (IV) *dimethyl bicyclo*[5,2,1,0 ^{2,6}]*deca*-3,8-*diene*-1,4-*dicarboxylate* (2·37 g.) (Found: C, 67·6; H, 6·7%; *M*, 252. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%; *M*, 248). Repeated chromatography of this material on silica gel from light petroleum gave first and last fractions whose infrared spectrum was identical with that of the starting material. The basic product from the dimethylamine treatment is a mixture of the dimethylamine adducts (V) and (VI) from Thiele's ester and the 103° isomer respectively; these adducts are separated by chromatography on silica gel, elution with light petroleum giving first the adduct (VI) (cf. below).

Properties of Thiele's Ester and Derived Compounds.—(*a*) The ester (II) was recovered unchanged after 15 minutes at 100° in absence of a solvent and after refluxing in methanol containing hydrochloric acid (100 moles %).

(*b*) The hydrogenation of the ester over Raney nickel at 1 atm. and room temperature has been described.[3] A dihydro-derivative (XXI), m. p. 86—87°, is obtained. A second dihydro-derivative, *dimethyl bicyclo*[5,2,1,0,^{2,6}]*dec*-4-*ene*-4,8-*dicarboxylate*, is formed when platinum is used as catalyst: this has m. p. 100° (Found: C, 67·1; H, 7·0%; *M*, 235. $C_{14}H_{18}O_4$ requires C,

67·2; H, 7·2%; *M*, 250). A mixture of the two dihydro-derivatives had m. p. 86—95°. Both isomers were crystallised to constant m. p. and infrared spectrum: both were recovered unchanged after reaction with dimethylamine under the usual conditions, and after being dissolved in methanolic sodium methoxide or sulphuric acid. The same tetrahydro-derivative (XXVI), m. p. 77°, was obtained on further hydrogenation of the two dihydro-derivatives.

(*c*) The dimethylamine adduct (V) of Thiele's ester has been described.[4] The parent ester was regenerated in about 50% yield by boiling the adduct with water for 10—15 min.: prolonged boiling gives a mixture.[4] The adduct (0·5 g.) and phenyl azide (0·5 g.) were kept in ethyl acetate (3 ml.) for 7 days, the solvent was removed *in vacuo*, and the residue washed with light petroleum (b. p. below 40°); the solid residue crystallised from light petroleum to give the starting adduct (0·18 g.) (mixed m. p. and infrared spectrum). Hydrogenation of the dimethylamine adduct (V) in ethanol over Raney nickel or platinum led to low and variable hydrogen uptake. Hydrogenation over platinum in dilute hydrochloric acid was better, but still rather erratic. The adduct (2·08 g.) in dilute hydrochloric acid (25 ml.) took up 166 ml. of hydrogen ($1H_2$ = 160 ml.) in 2 hr. The catalyst coagulated at the end of the hydrogenation and was removed from the solution as soon as the reaction was complete. The basic product, *9-dimethylaminobicyclo*[5,2,1,$0^{2,6}$]*decane-4,8-dicarboxylate* (XXV) had m. p. 82—84° after several crystallisations from light petroleum (Found: C, 65·0; H, 8·4; $C_{16}H_{25}NO_4$ requires C, 65·1; H, 8·5%. Nitrogen analyses were low and variable) and had no intense ultraviolet absorption above 210 mμ. Removal of the dimethylamine by refluxing this dihydro-derivative (1·0 g.) with water (10 ml.) for 15 min. gave as the neutral product, *dimethyl bicyclo*[5,2,1,$0^{2,6}$]*dec-8-ene-4,8-dicarboxylate* (XXII), an oil (0·52 g.) (Found: C, 67·35; H, 7·3. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). The phenyl azide adduct was prepared by keeping a solution of compound (XXII) (0·45 g.) in phenyl azide (0·5 g.) for 24 hr. and then removing the excess of azide by light petroleum (b. p. below 40°). The solid residue of *dimethyl 9-phenylazidobicyclo*[5,2,1,$0^{2,6}$]*decane-4,8-dicarboxylate* (0·3 g.), crystallised from a small volume of methyl acetate, had m. p. 125—140° (Found: C, 63·9 H, 6·5 N, 11·8. $C_{20}H_{23}N_3O_4$ requires C, 65·0; H, 6·3; N, 11·4%).

Properties of the Isomer (III) *and its Derivatives.*—The dimethylamine adduct (VI) was prepared by keeping a solution of the 103° isomer (0·15 g.) in dimethylamine (2 ml.) overnight, removing the excess of amine *in vacuo* and crystallising the *product* (0·13 g.) from light petroleum. It had m. p. 127—128° (Found: C, 65·3; H, 7·4; N, 5·4%; *M*, 287. $C_{16}H_{23}NO_4$ requires C, 65·5; H, 7·9; N, 4·8%; *M*, 293) and showed only ester absorption in the ultraviolet region. A solution of this adduct (0·02 g.) in phenyl azide (0·1 g.) was kept for 24 hr.; the infrared spectrum of the basic product from this reaction (0·014 g.) was identical with that of the starting material.

Properties of the Liquid Isomer (IV) *and its Derivatives.*—(*a*) Hydrolysis of the liquid ester (0·55 g.) by refluxing it with sodium hydroxide (0·5 g.) in water (10 ml.) for 45 min. and precipitation of the acid by acidification gave the free acid (0·41 g.), having m. p. 201° (lit.,[6] 201°) after one crystallisation from a large volume of butyl acetate (Found: C, 65·55; H, 5·5%; equiv. 109. Calc. for $C_{12}H_{12}O_4$: C, 65·45; H, 5·55%; equiv., 110). Re-esterification of the acid by refluxing it with methanol containing a little sulphuric acid regenerated the liquid isomer, having the original infrared spectrum.

(*b*) Hydrogenation of the liquid isomer (0·97 g.) in ethanol (20 ml.) over platinum at 1 atm. and room temperature led to the rapid uptake of 92 ml. of hydrogen ($1H_2$ = 87 ml.). The rate of hydrogen uptake then fell markedly. The product (0·84 g.) was *dimethyl bicyclo*[5,2,1,$0^{2,6}$]-*dec-3-ene-1,4-dicarboxylate* (XXIII) (Found: C, 66·7; H, 7·4. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). This dihydro-derivative (0·25 g.) was recovered unchanged in infrared spectrum after being kept in phenyl azide (0·25 g.) for 24 hr.

(*c*) The liquid isomer (1·0 g.) was depolymerised quantitatively by distillation at 10 mm. (bath-temp. 160°, vapour-temp. 100—120°) to give a colourless oil whose infrared and ultraviolet spectra were those of methyl cyclopentadiene-1-carboxylate obtained by depolymerising Thiele's ester. After spontaneous dimerisation at room temperature for 24 hr., the product mixture (0·65 g.) had an infrared spectrum identical with that of the dimerisation mixture of methyl cyclopentadiene-1-carboxylate; crystallisation of this mixture from light petroleum gave Thiele's ester (0·30 g.), m. p. and mixed m. p. 83—85°.

Miscellaneous Compounds.—The filtrate from the light petroleum crystallisation of the crude ester (Ziegler *et al.*[7]) gave an oil (18 g.) which was dissolved in dimethylamine and kept for 24 hr. at 0°. The neutral product from this mixture was a semi-solid mixture of the liquid isomer

(IV) and the adduct (XXIV). Washing with light petroleum (b. p. below 40°) removed the oil, leaving *dimethyl 9-methoxybicyclo*[5,2,1,$0^{2,6}$]*dec-4-ene-4,8-carboxylate* (XXIV) (2·5 g.), m. p. 111° (from light petroleum) (Found: C, 64·3; H, 7·1%; *M*, 261. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·2%; *M*, 280). Mixtures of this compound, the isomer (III), and the dimethylamine adduct of Thiele's ester were molten below 95°. After compound (XXIV) (0·3 g.) had been kept with phenyl azide (0·3 g.) in ethyl acetate (3 ml.) for 7 days, it was recovered (0·22 g.) unchanged in m. p., mixed m. p., and infrared spectrum.

Compound (XXIV) (0·5 g.) and sodium hydroxide (0·5 g.) in water were refluxed for 30 min. Acidification gave Thiele's acid (0·32 g.), m. p. and mixed m. p. 211—212° (from butyl acetate). Esterification of this acid gave Thiele's ester (m. p., mixed m. p., infrared spectrum).

Compound (XXIV) was unaffected when refluxed with water for 30 min.

Compounds (XXV—XXVIII) were obtained by hydrogenation of available compounds. Compound (XIV) was prepared as already described;[9] the product had no 13·05 μ band as reported[8b] for the *exo*-analogue.

Kinetics.—The rate of dimerisation of methyl cyclopentadiene-1-carboxylate was measured by the rate of disappearance of the monomer peak at 270 mμ. It is not possible to determine an accurate ε value for the monomer, since a sample may contain up to 20% of dimer. The ε value was estimated as 7500 at 270 mμ, by distilling Thiele's ester (1·0 g.) into a weighed receiver, adding 20 ml. of ethanol from a calibrated pipette, and weighing the whole before recording its ultraviolet spectrum. The resulting ε value (6250) was increased by 20% since the infrared spectrum of this material showed bands corresponding to this concentration of the dimer. This uncertainty in ε is reflected in the absolute value of the rate constants and so in the pre-exponential Arrhenius *A* factor.

In a typical kinetic run, Thiele's ester (*ca.* 2·0 g.) was distilled into a receiver at −80° and the resulting monomer was made up to 50 ml. and kept at 30° (thermostat). Samples were withdrawn at intervals and diluted 2500 times to produce an optical density of 0·1—0·6 at 270 mμ. Beer's law is obeyed by the monomer over this concentration range. The second-order velocity constants (l. $mole^{-1}$ $sec.^{-1}$) are: at 0°, $2·5 \times 10^{-5}$; at 30°, $3·8 \times 10^{-4}$; at 50°, $1·5 \times 10^{-3}$. The Arrhenius plot is linear; the activation energy is 14·7 kcal. $mole^{-1}$, and log *A* 7·4. The first- and third-order plots of the kinetic runs are curved. The dimer peak at 220 mμ does not show a simple behaviour during the kinetic run, probably because the monomer also absorbs to an unknown extent at this wavelength.

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[*Received, August 5th*, 1960.]

[9] (*a*) Bruson and Reiner, *J. Amer. Chem. Soc.*, 1945, **67**, 723; cf. Wilder, Culbertson, and Youngblood, *ibid.*, 1959, **81**, 656; (*b*) Cristol, Seifert, and Soloway, *ibid.*, 1960, **82**, 2351.

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212. *Heats of Sublimation of Straight-chain Monocarboxylic Acids.*

By MANSEL DAVIES and V. E. MALPASS.

The sublimation pressures of the even-carbon monocarboxylic acids from C_{10} to C_{32} have been measured by the effusion method down to 10^{-5} mm. so as to give reliable values of the sublimation heats. Both the heats and entropies of sublimation increase linearly with chain length. The significance of the additive increments and the constant terms in these relations is discussed with reference to other similar data. Infrared absorption spectra were used as a check on the polymorphic forms of the acids, and small features peculiar to the C_{12} and the C_{20} acid are taken to be correlated with the deviations of these acids from the linear sequences formed by the others.

THE lattice energy of a compound can be equated to its heat of sublimation provided (i) that there is no significant change in the configuration of the molecules on change of state; (ii) that the energies associated with molecular vibrations remain unchanged;

(iii) that the vapour in equilibrium with the solid behaves ideally. The sublimation heat can be determined from the temperature variation of the sublimation pressure. The latter has been measured for the even carbon-number monocarboxylic acids from C_{10} to C_{22} inclusive.

Experimental

The acids used were those described by Stenhagen and von Sydow: the m. p.s agreed satisfactorily with those in ref. (1). To obtain immediately comparable values of the heats and entropies of sublimation the same polymorphic form of the homologues should be measured.

Table 1. *Observed sublimation pressures.*

(*a*) n-Decanoic acid (C_{10}): $\log_{10} p$ (mm.) = 17·130 − 6119/T

t (°c)	27·83	27·60	27·55	25·55	22·80	22·00	20·00	16·80
10^4p (mm.), obs....	6·56	6·25	5·74	4·49	2·89	2·47	1·84	$1·07_5$
Devn. (%)	+3·2	+1·2	−4·3	+0·4	+0·0	−1·6	+1·3	+0·0

(*b*) n-Dodecanoic (C_{12}): $\log_{10} p$ (mm.) = 19·897 − 7322/T

t (°c)	41·44	41·44	41·44	41·35	39·54	35·20	30·20	29·70	22·70
10^4p (mm.), obs....	4·07	4·29	4·01	4·31	3·04	1·53	0·570	0·548	0·139
Devn. (%)	−2·5	+2·6	−4·1	+4·9	+0·1	+7·8	−1·7	+2·6	−1·4

(*c*) n-Tetradecanoic acid (C_{14}): $\log_{10} p$ (mm.) = 18·740 − 7291/T

t (°c)	52·17	52·14	49·39	46·85	44·90	42·65	38·85
10^5p (mm.), obs....	$21·3_5$	$21·2_1$	14·5	8·3	$6·5_2$	$4·3_5$	$2·4_5$
Devn. (%)	−0·9	−0·5	+5·8	−7·9	−0·6	−2·4	+3·8

(*d*) n-Hexadecanoic acid (C_{16}): $\log_{10} p$ (mm.) = 20·217 − 8069/T

t (°c)	60·14	59·19	57·89	56·94	55·29	51·19	46·64
10^5p (mm.), obs.	$10·0_4$	8·80	7·05	6·14	4·75	2·16	0·98
Devn. (%)	−1·8	−0·1	±0·0	+1·1	+5·2	−3·3	+1·4

(*e*) n-Octadecanoic acid (C_{18}): $\log_{10} p$ (mm.) = 21·180 − 8696/T

t (°c)	67·19	66·89	66·09	64·89	62·79	61·99	57·89
10^5p (mm.), obs....	4·28	4·17	3·46	3·06	1·94	1·69	$0·82_7$
Devn. (%)	+0·1	+1·5	−1·1	+7·0	−2·6	−0·5	+1·5

(*f*) n-Eicosanoic acid (C_{20}): $\log_{10} p$ (mm.) = 25·453 − 10424/T

t (°c)	72·90	72·60	69·99	68·50	68·50	66·25	63·80	63·80
10^6p (mm.), obs....	21·0	20·9	12·2	$8·2_4$	$8·7_9$	$5·3_6$	$2·9_2$	$3·8_6$
Devn. (%)	−3·6	+3·1	−0·4	−5·8	+0·5	−3·2	−12·8	+15·2

(*g*) n-Docosanoic acid (C_{22}): $\log_{10} p$ (mm.) = 23·604 − 10102/T

t (°c)	78·56	77·93	76·67	75·86	74·75	72·67	71·60
10^6p (mm.), obs....	7·9	$6·6_1$	$5·6_3$	$4·5_8$	$3·8_5$	$2·4_2$	$2·0_8$
Devn. (%)	+3·4	−3·0	+1·9	−0·1	+3·5	−3·2	+2·4

As, owing to the low sublimation pressures, all the measurements were necessarily made at temperatures adjacent to the m. p., the acids were carefully melted and resolidified near their m. p. This should have ensured that they were each in the *C*-form.[1]

The sublimation pressures were determined by Knudsen's effusion method, details of which have been given.[2] The weights effused were determined on an Oertling air-damped microbalance with an uncertainty of ±10 μg. Effective hole diameters were determined by measurements at temperatures of 29—39° by using benzophenone [3] or at 50—70° by using benzoic acid,[4] the ranges and mean values of the observed areas (cm.²) being 23·7 ± 0·3 × 10^{-3}, 7·23 ± 0·06 × 10^{-3}, 1·24 ± 0·03 × 10^{-3}. For the C_{22} acid the effusion of 250 μg. in 10 hr. corresponded to a sublimation pressure of 5 × 10^{-6} mm. In addition to the checks already described,[2] it is noteworthy that the residual pressure is unlikely to influence significantly the determination of such low values. From Binks and Bradley's study,[5] a residual air pressure as high as 10^{-2} mm. would change the rate of effusion by only about 1%.

[1] Stenhagen and von Sydow, *Arkiv Kemi*, 1953, **6**, 310.
[2] Davies, A. H. Jones, and Thomas, *Trans. Faraday Soc.*, 1959, **55**, 1100.
[3] Neumann and Volker, *Z. phys. Chem.*, 1932, **161**, 33.
[4] Davies and J. I. Jones, *Trans. Faraday Soc.*, 1954, **50**, 1042.
[5] Binks and Bradley, *Proc. Roy. Soc.*, 1949, *A*, **198**, 231.

Thermometers calibrated in the N.P.L. were used, and any necessary corrections applied after thermostat temperatures had been read.

Infrared spectra were run in a heated cell having a similarly heated compensator, whose temperature was controllable to $\pm 1°$. The Grubb–Parsons G.S.3 double-beam grating instrument was used, and the region 670—2000 cm.$^{-1}$ (15—5 μ) systematically recorded under standardized conditions.

Results.—The data for each compound were plotted as log p(sub.) against $1/T$. It was frequently found that some of the determinations first made near the m. p. with a new compound were abnormally high. They were repeated until satisfactory reproducibility showed that the volatile impurities (very probably moisture) were no longer noticeable. After rejection of any such early points, the " least-squares " line from the remaining observations was calculated, the origin of co-ordinates being first brought to the " centre of gravity " of the points. The data are summarized in the Tables, where " Devn. (%) " is 100 [p(obs.) − p(calc.)]/p(calc.) and p(calc.) is the value given by the equation quoted.

TABLE 2. *Heat and entropies of sublimation.*

No. of C atoms	Temp. range studied (°C)	No. of dtmns.	ΔH (obs.) (kcal. mole^{-1})	ΔH (calc.) (kcal. mole^{-1})	ΔS (obs.) (cal. mole^{-1} deg.$^{-1}$)	ΔS (calc.) (cal. mole^{-1} deg.$^{-1}$)
10	16·80—27·83	8	28·0 ± 0·4	27·7	65·2 ± 1·5	64·6
12	22·70—41·44	9	33·5 ± 0·8	30·7	77·9 ± 3·0	69·4
14	38·85—52·17	7	33·4 ± 0·9	33·7	72·6 ± 3·5	74·2
16	46·64—60·14	7	36·9 ± 1·0	36·7	79·3 ± 4·0	79·0
18	57·89—67·19	7	39·8 ± 1·0	39·7	83·7 ± 3·0	83·8
20	63·80—72·90	8	47·7 ± 1·8	42·7	103·3 ± 4·5	88·5
22	71·60—78·56	7	46·2 ± 1·9	45·7	94·8 ± 5·0	93·4

DISCUSSION

Addivity of Enthalpy and Entropy Factors.—The results for the individual acids conform in each case fairly well to linearity between $\log_{10} p$ (sub.) and $1/T$. For the C_{20} and the C_{22} acid the weights effusing in 8 hr. were usually less than 500 μg.; an uncertainty of $\pm 2\%$ was then expected in individual determinations of these sublimation pressure. We have, in terms of the equation $\log_{10} p$ (mm.) $= A + B/T$:

$$\Delta H \text{ (sub.)} = -2{\cdot}303\boldsymbol{R}B$$
$$\Delta S \text{ (sub.)} = 2{\cdot}303\boldsymbol{R}(A - 2{\cdot}8808)$$

After representing the probable uncertainties of individual points in the log p–$1/T$ plot, generous estimates of the likely limits for the resultant ΔH and ΔS values are given in Table 2. At pressures of *ca.* 30 mm. and temperatures similar to ours, the lower carboxylic acids show only some 10—20% of the molecules to be dimeric in the vapour.[6] As all the sublimation pressures were less than 10^{-3} mm., it seems safe to conclude that the vapours were then essentially ideal. The experimental ΔH values thus provide, to almost within their significance, a measure of the lattice energies.

The simple expectation that the lattice energy may be proportional to the chain-length is well substantiated. In Table 2, ΔH (calc.) are the values, in kcal. mole^{-1}, derived from

$$\Delta H \text{ (sub.)} = 14{\cdot}2 + 1{\cdot}50(n - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the acid is $C_{n-1}H_{(2n-1)}{\cdot}CO_2H$. For all but C_{12} and C_{20} the deviation from the " best " observed values is within 1%. The two exceptions will be discussed later. Not surprisingly, a similar relation is found for the molar entropy of sublimation, in cal. mole^{-1} deg.$^{-1}$:

$$\Delta S \text{ (sub.)} = 43{\cdot}0 + 2{\cdot}4(n - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[6] Taylor, *J. Amer. Chem. Soc.*, 1951, **73**, 315; 1952, **74**, 4151.

This is the relation which gives the ΔS (calc.) of Table 2, and, by using the units of cal. mole^{-1} deg.$^{-1}$ for ΔS and kcal. mole^{-1} for ΔH, the sublimation parameters are related by

$$\Delta S = 20{\cdot}3 + 1{\cdot}60\Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The values of ΔS given by the linear equation (3) are, with the exceptions of those for C_{12} and C_{20}, all within 2% of ΔS (obs.), the average deviation being only 0·7%. This simple interdependence emphasizes that, for the five compounds concerned, the sublimation process follows a strictly uniform pattern, the energy involved depending simply on the enhancement of the configurational freedom which is attained. It is for such phase changes, and homologous series of compounds, that these additivities and linear relations of the thermodynamic parameters [7] are most likely to arise.

Equation (1) is of particular interest as it shows the constant contribution of 1·50 kcal. mole^{-1} by each CH_2 group to the lattice energy. In some long-chain primary amides the value of 1·72 kcal. mole^{-1} has been found for this factor,[2] 1·66 kcal. mole^{-1} in some *N*-methylamides,[8] and 1·62 kcal. mole^{-1} in straight-chain dicarboxylic acids.[9] The " constant " term of 14·2 kcal. mole^{-1} represents the residuum in the lattice energy when the contribution of the $(n - 1)$ CH_2 groups has been removed, *i.e.*, it includes the difference between the CH_3 and CH_2 groups and the totality of the contribution by the CO_2 group. In the normal paraffins,[10] the CH_3 and CH_2 groups contribute 2·25 and 1·7 kcal. mole^{-1} to the heats of vaporization: their contributions might differ by 1 kcal. mole^{-1} in the sublimation heat. Accordingly, 13·2 kcal. mole^{-1} is a reasonable estimate for the CO_2H group contribution.

This large term includes the energy of one of the hydrogen bonds formed by the dimerization of the carboxyl groups. As has already been pointed out,[2,4] it necessarily includes items other than those localized in the (O–H $\cdots$ O) interaction. A more significant estimate of this hydrogen-bond energy in the solid will become available when we can subtract from 13·2 kcal. mole^{-1} the lattice energy term for a non-associated carboxyl group. It should be possible to estimate this from the data for a series of increasingly " hindered " carboxylic acids. The possibility remains that the hydrogen-bond energy in these instances may be at least as large as in the vapour state (*ca.* 7 kcal. mole^{-1}), despite the fact that the medium (*via* its dielectric constant and other factors) usually greatly reduces the energy.[11] Maximum interaction can be expected in the solid state from the fixed orientations imposed in the crystal: there the sequence in interaction energy values characteristic of free gas molecules, *viz.*, dispersion > induction $\geqslant$ dipole, can be reversed, *e.g.*, as the dipole term becomes proportional to (distance)$^{-3}$.

There are some other values which can be compared with the constant term of 14·2 kcal. mole^{-1} for these aliphatic acids. In the straight-chain dicarboxylic acids [9] the same factor is 12·2 kcal. mole^{-1}: in some benzoic acids [4] it is 11·5 kcal. mole^{-1}. These variations are probably expressions of the non-localized factors and of the influence of the environment upon the net interaction energies of the carboxyl groups. There is no clear evidence that the geometry of the carboxyl group interactions differs in these instances: thus the (O–H $\cdots$ O) distance is the same [12] in crystalline benzoic as in succinic acid (2·64 Å). Other total head-group interactions to be compared with 14·2 kcal. mole^{-1} for the crystalline aliphatic acids are (in kcal. mole^{-1}): 17·6 for primary amides (two hydrogen bonds per molecule), 8·0 for some *N*-methylamides, 5·7 for the hydroxyl group in phenols,[11] and *ca.* 9 for the same group in supercooled liquid alcohol structures.[10] As could be expected

[7] Cf. Janz, " Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, New York, 1958.
[8] Davies and A. H. Jones, *Trans. Faraday Soc.*, 1959, **55**, 1329.
[9] Thomas, M.Sc. Thesis, University of Wales, 1959.
[10] (*a*) Moelwyn-Hughes, " Physical Chemistry," Pergamon Press, London, 1957; (*b*) Davies, *J. Polymer Sci.*, 1959, **40**, 247.
[11] Davies, in " Hydrogen Bonding," ed. D. Hadži, Pergamon Press, London, 1959.
[12] " Interatomic Distances," ed. Sutton, *Chem. Soc. Special Publ.* No. 11, 1958.

from other data, the hydrogen bond in the carboxylic acids is the strongest of these examples.

Anomaly of C_{12} *and* C_{20} *Factors.*—Clearly, the data for the C_{12} and the C_{20} acid do not fit into the foregoing pattern: the deviations from the linear relations are far larger than the uncertainties in the individual ΔH and ΔS values. For the C_{12} acid two specimens were studied with essentially identical results. The only likely explanation of these findings is that they relate to some slight difference in the crystalline *C*-form pertaining to these acids. The established transition points [1] indicate that the *C*-forms are stable for a range of 12° below the m. p. for C_{12} and for 23° below the m. p. for C_{20}, thus including all but the lowest determinations for the C_{12} acid. Again, the *C*-forms are usually produced from the melt or by rapid cooling of a solution. They can be described as metastable below the transition temperatures and it has been found [13] that the C_{12} and the C_{14} acid revert to the *A*-form when kept for two years at room temperatures. Even then, heating to within a few degrees of the m. p. produced the *C*-form. It was these observations that gave us preliminary confidence that the acids would all be isomorphous in the sublimation-pressure measurements.[14]

Table 2 shows the observed ΔH (sub.) for C_{12} and C_{20} to be 2·8 and 5·0 kcal. mole^{-1} above the figures expected for the *C*-forms. Per chain-carbon CH_2 in these acids, the deviation is sensibly constant (0·25 and 0·26 kcal. mole^{-1}). That this is a reasonable difference for a polymorphic change is perhaps indicated by the varying lattice-energy increments per CH_2 in various established sequences: in kcal. mole^{-1} the even-carbon dicarboxylic acids give 1·71; the lower odd-carbon primary amides 1·20; the lower even-carbon primary amides 1·02; and (above) the acids, 1·50. For a series of long-chain (odd-carbon) carboxylic acids, Garner *et al.*[15] found heats of transition between polymorphic forms of 1—2 kcal. mole^{-1}. The fact that these heats of transition showed little dependence on chain length suggests that they were principally concerned with different head-group interactions, as is confirmed by the constant angle of tilt for their hydrocarbon chains (59° 12′). More significantly, when the ethyl esters of the even monocarboxylic acids change the tilt of their chains from 90° to about 66°, then the heat of transition is 4·87 kcal. mole^{-1} for the C_{18} compound and it increases for each successive $(CH_2)_2$ added by 0·59, 0·65, 0·54, 0·69 kcal. mole^{-1}, or a mean value of 0·31 kcal. mole^{-1} per CH_2 group.[15] This is similar to the deviation shown in our data by C_{12} and C_{20}. It will be of some interest to confirm the ΔH values now suggested for possible polymorphic transformations in the C_{12} and C_{20} acid.

Infrared Study of the Crystalline Acids.—A direct examination for any obvious phase changes can be made from the infrared absorption spectra of the solid acids.[16] A systematic check for all the acids was made. A difficulty here is that of ensuring the same form in the infrared examination as was present at each stage of the sublimation measurements. In practice the acids were each melted between rock-salt plates and the films (both liquid and solid) examined after being kept for various times at temperatures between the m. p. and 25° in an appropriately heated infrared absorption cell. In this way it was hoped to simulate the conditions in the sublimation work.

In these circumstances none of the solid acids showed marked changes in the infrared absorptions between their m. p. and 25°, even when kept for periods up to a week: considerable changes in detail occurred on melting but the same solid form reappeared on cooling. For the solids, such changes as occurred with temperature or time were smaller than would betoken a phase change in the compounds. One consistent feature was the

[13] Lomer, *Nature*, 1955, **176**, 653.
[14] See also Malkin, "Progress in Chemistry of Fats and other Lipids," Vol. I, Pergamon Press, London, 1952, p. 10.
[15] See Ralston, "Fatty Acids and their Derivatives," John Wiley and Sons, New York, 1948, pp. 344, 355, 362.
[16] R. N. Jones *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 2570; von Sydow, *Acta Chem. Scand.*, 1955, **9**, 1119.

progressive reduction in the resolution of the doublet absorption at 720—728 cm.$^{-1}$ found in all these acids: as the temperature approached the m. p. the higher-frequency component was sometimes reduced in relative intensity and the trough between them invariably became less pronounced. The broad absorption centre near 940 cm.$^{-1}$ in all the acids also showed minor changes, in the form of somewhat sharper shoulders as the temperature decreased.

The spectra of the different acids have also been compared with a view to assess the similarity of the crystalline forms. The spectra are all nearly identical, apart from the well-established increase in the number of sharp absorptions between 1180 and 1340 cm.$^{-1}$ as the number of CH_2 groups in the chain increases. There are, however, features between 670 and 1000 cm.$^{-1}$ which distinguish the C_{12} and C_{20} from the other acids. This is illustrated in Figs. 1 and 2, where the records (on a linear wavelength scale) for C_{12} and C_{20}

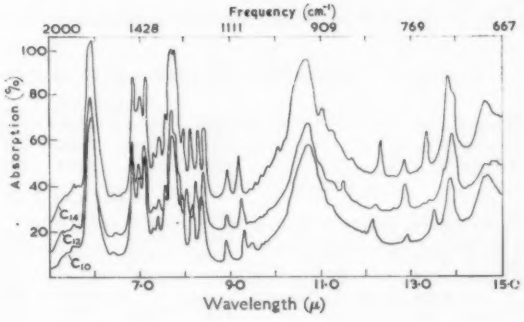

FIG. 1. *Absorptions of crystalline films of n-aliphatic acids at 25°. (For C_{14} the absorptions are displaced upwards by 20%.)*

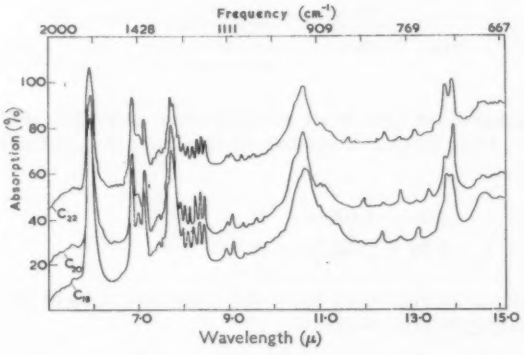

FIG. 2. *Absorptions of crystalline films of n-aliphatic acids at 25°. (For C_{20} the absorptions are displaced upwards by 20%, and for C_{22} by 40%.)*

are compared with those for the immediately lower and higher even acids: C_{12} shows a sharp absorption at 871 cm.$^{-1}$ (11·48 μ) not present in C_{10} or C_{14} and it lacks all but a trace of the peak near 816 cm.$^{-1}$ (12·25 μ) present in its neighbours; the 779 cm.$^{-1}$ (12·84 μ) feature in C_{12} is much stronger than in C_{10} or C_{14}, and C_{12} fails to show the equivalent of the well-defined absorptions near 746 cm.$^{-1}$ (13·4 μ) in C_{10} and C_{14}. These changes are in minor features of the solid-state spectra but they are significant in the present circumstances in that C_{12} appears to depart slightly from the very closely similar infrared fingerprints of C_{10} and C_{14}. As Fig. 2 illustrates, C_{20} shows similar small deviations from its nearest neighbours in the even-acid series: the C_{20} solid shows distinct absorptions at 835 cm.$^{-1}$ (11·97 μ) and 746 cm.$^{-1}$ (13·4 μ) not present in C_{18} or C_{22}, whilst the 781 cm.$^{-1}$ (12·8 μ) feature in C_{20} is much more pronounced than in C_{18} or C_{22}; conversely, the latter both show absorptions near 870 cm.$^{-1}$ (11·5 μ) and 763 cm.$^{-1}$ (13·1 μ) which are much reduced or absent in C_{20}.

Such changes probably mean only small differences in the force fields of the molecules in the crystal lattice but, when multiplied by the number of CH_2 groups involved, they might correspond to the anomalies observed in the lattice energies of C_{12} and C_{20}. At least there is a qualitative indication in that sense.

The identity of the forms whose spectra we have recorded is established by comparison with the published accounts of the alternative forms for palmitic (C_{16}) and stearic (C_{18}) acids.[16] Our spectra were run fairly rapidly, and both that and the natural widths of some of the solid phase absorptions do not allow us to expect an accuracy of better than ± 3 cm.$^{-1}$ for our measurements. All of von Sydow's and most of Jones's spectra relate to Nujol mulls, which may itself be the source of some differences: owing to the Nujol absorptions their records show gaps on either side of 1430 cm.$^{-1}$. Using the features singled out by von Sydow as discriminating between the various spectra, the comparisons in Table 3 show our solid acids to be in the *C*-form. (Our reading of cm.$^{-1}$ from the curves of R. N. Jones *et al.* might itself be in error by ± 2 cm.$^{-1}$.)

TABLE 3. *Comparison of discriminating absorptions (cm.$^{-1}$) in polymorphic forms.*

Palmitic acid (C_{16})									
Present work	1695	1405	1298	1269	1248	1225	1206	1188	941
C-form (E. v. S.)	1701	1412	1294	1271	1250	1226	1205	1187	939
A-form (E. v. S.)	1698	1408	1295	1271	1252	1230	1209	1197	935
Stearic acid (C_{18})									
Present work	1691	1408	1297		1255		1238		
C-form (E. v. S.)	1701	1414		1282	1263	1243			
B-form (E. v. S.)	1701	1403	1290	1276	1264	1248			
C-form (R. N. J. *et al.*)	1698	1409	1292		1258		1235		
B(+ *C*) form (R. N. J. *et al.*)	—	—	1298	1284	1269	1263	1237		
Present work	1218	1200	1186	951(sh)		937(centre)			
C-form (E. v. S.)				952(sh)		941(centre)			
B-form (E. v. S.)				941(sh)		887(centre)			
C-form (R. N. J. *et al.*)	1217		1182	958		937(centre)			
B(+ *C*) form (R. N. J. *et al.*)	1219					884(centre)			

The additivity of some energy factors other than heats of sublimation is already well established for the carboxylic acids. Thus Ralston [17] quotes, in the units of equations (1) and (2) for the even mono-acids:

$$\Delta H \text{ (melting)} = -2{\cdot}58 + 1{\cdot}030(n - 1)$$
$$\Delta S \text{ (melting)} = -1{\cdot}65 + 2{\cdot}652(n - 1)$$

From these (only rough approximations) by difference from the equations (1) and (2), the corresponding values for the vaporization process are:

$$\left.\begin{aligned} \Delta H \text{ (vap.)} &= 16{\cdot}9 + 0{\cdot}47(n - 1) \\ \Delta S \text{ (vap.)} &= 44{\cdot}6 - 0{\cdot}26(n - 1) \end{aligned}\right\} \quad \ldots\ldots \quad (4)$$

These values will only obtain near the m. p. and only in so far as the vapour behaves ideally.

The values suggested by equation (4) may be compared with those calculated directly from the few vapour-pressure measurements (0·2—1 mm.) by Jantzen and Erdmann: [18] the uncertainty in their ΔH (obs.) values is at least $\pm 0{\cdot}5$ kcal. mole^{-1}. [The most extensive data of Spizzichino [19] lead to ΔH (vap.) values varying by $\pm 20\%$ in a negligible temperature range.] The agreement in Table 4 is better than could have been expected.

[17] Ralston, ref. 15, p. 325.
[18] Jantzen and Erdmann, *Fette und Seifen*, 1952, **54**, 197.
[19] Spizzichino, *J. Récherches C.N.R.S.*, 1956, No. 34.

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TABLE 4. *Comparison of predicted and observed heats of vaporization of the liquid acids near their m. p.s (kcal. mole^{-1}).*

Acid	C_{14}	C_{16}	C_{18}	C_{22}
ΔH (vaporization, eqn. 4)	23·0	24·0	24·9	26·8
ΔH (obs.) [18]	23·0	24·8	24·3	26·6

For a limited number of the monocarboxylic acids, the heats of solution in water at 55° in kcal. mole^{-1} are approximately [10b]

$$\Delta H \text{ (solution in } H_2O \text{ at } 55°) = -4{\cdot}60 + 1{\cdot}03(n - 1)$$

From this and equation (1) one finds for the heat of solvation, *i.e.*, for the process

Carboxylic acid in dilute vapour ⟶ carboxylic acid in saturated aqueous solution at 55°,

$$\begin{aligned}\Delta H \text{ (solvation in } H_2O \text{ at } 55°) &= \Delta H \text{ (solution)} - \Delta H \text{ (sublimation)} \\ &= -18{\cdot}8 - 0{\cdot}47(n - 1)\end{aligned}$$

If the water is replaced by glacial acetic acid as the solvent, the heat of solution is less dependent on temperature and we find [10b]

$$\Delta H \text{ (solvation in glacial acetic acid)} = -45{\cdot}6 + 2{\cdot}64(n - 1)$$

These relations can be of value both in estimating unknown parameters for these compounds and in revealing the extent of the contributions to the factors by the component groups in such compounds. The large energies made available by the solvation of the carboxylic group are noticeable and, for the glacial acetic acid solutions, remarkable.

We acknowledge a grant from the Chemical Society and a Maintenance Award to V. M. from the D.S.I.R. We particularly thank Professor E. Stenhagen of Göteborg University for samples of the pure acids.

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213. *The Structure of Products Derived from Tazettine with Acetic Anhydride and Sulphuric Acid.*

By YOSHISUKE TSUDA and SHOJIRO UYEO.

The structure (VII; R = H, R′ = OAc) is advanced for the "neutral compound" obtained by Kondo when tazettine was treated with acetic anhydride in the presence of sulphuric acid. The generality of this reaction was tested upon dihydrotazettine, dihydroisotazettinol, dihydrotazettinol, and demethoxydihydrotazettine.

TAZETTINE, an alkaloid occurring in the Amaryllidaceæ, has been shown [1,2] to have structure (I; R = OMe, R′ = H, R″ = OH), containing a β-oxopyrrolidine moiety in which the carbonyl group is masked by forming a hemiketal arrangement.* It is conceivable that the methylene group between the nitrogen atom and the masked carbonyl group should be vulnerable to oxidation. However, oxidative studies of tazettine

* That the configuration of the hemiketal hydroxyl group is as formulated will be conclusively shown in a forthcoming paper.

[1] Ikeda, Taylor, Tsuda, Uyeo, and Yajima, *J.*, 1956, 4749.
[2] Irie, Tsuda, and Uyeo, *J.*, 1959, 1446.

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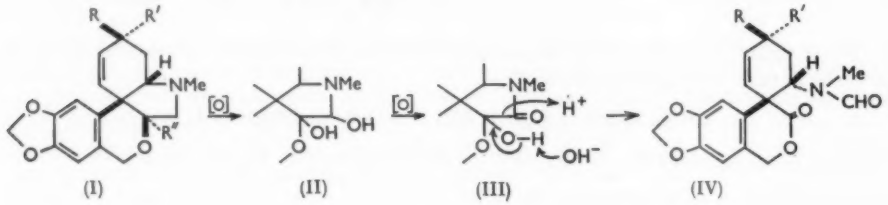
have led to a complex of products except where manganese dioxide was used as a reagent.[1,3] The main product in that case was the amido-lactone (IV; R = OMe, R′ = H) which was presumably produced by cleavage of an intermediate (III), which was formed in turn from the primary product, the carbinolamine (II).



(I) (II) (III) (IV)

The free hydroxyl group of the hemiketal moiety must play an important rôle in accelerating this type of oxidation because when it was masked by acetylation, as in acetyltazettine (I; R = OMe, R′ = H, R″ = OAc), diacetyltazettinol (I; R = R″ = OAc, R′ = H), or diacetylisotazettinol (I; R = H, R′ = R″ = OAc), the oxidation did not proceed to any noticeable extent.

This paper is concerned with tazettine derivatives containing an oxygenated methylene grouping at the above-mentioned position.

Späth and Kahovec[4] prepared acetyltazettine (I; R = OMe, R′ = H, R″ = OAc) by the action of acetic anhydride on tazettine in the presence of a few drops of sulphuric acid in the cold. Kondo and Ikeda[5] later reported failure to reproduce this preparation, as they obtained a neutral compound, m. p. 254° (decomp.), together with a diacetate, m. p. 137—140°, but no acetyltazettine. In view of this discrepancy, acetylation of tazettine with acetic anhydride and sulphuric acid was re-investigated. It was found that when the quantity of the sulphuric acid added to a mixture of tazettine and acetic anhydride was so small that some starting material was recovered unchanged, the only isolable product was the normal acetylation product of tazettine (Späth's product). When the amounts of sulphuric acid were increased, however, acetyltazettine was no longer isolable and Kondo and Ikeda's products were obtained. The yield of the neutral fraction could be increased to a maximum of 90% by increasing the proportion of sulphuric acid to anhydride. The " diacetate " was found to be a mixture of diacetyltazettinol[1] (I; R = R″ = OAc, R′ = H) and diacetylisotazettinol[1] (I; R = H, R′ = R″ = OAc) in a ratio of about 1 : 2, and these were separated by chromatography. The neutral fraction was also found to be a mixture which consisted principally of a crystalline compound, acetyldehydroisotazettinol, m. p. 263° (decomp.). Identity of this with the " neutral compound " of Kondo and Ikeda was confirmed by comparison of the infrared spectra. From the mother-liquors another compound, acetyldehydrotazettinol, m. p. 204—207°, was isolated in pure crystalline form only after chromatography over alumina and silica gel.

Analyses indicated that acetyldehydroisotazettinol has the empirical formula $C_{19}H_{19}O_6N$ rather than $C_{20}H_{25}O_6N$ attributed to it by the earlier authors.[5] It contained one acetyl but no methoxyl group. The infrared spectrum did not show the presense of a hydroxyl group, and the ultraviolet absorption spectrum revealed that no double bond was conjugated with the benzene ring. Alkaline hydrolysis yielded a deacetyl compound, dehydroisotazettinol, m. p. 264° (decomp.), which was also very weakly basic and exhibited a sharp hydroxyl band in the infrared spectrum at 3425 cm.$^{-1}$, but neither acetyl nor other carbonyl bands in the carbonyl region. Dehydroisotazettinol did not depress

[3] Highet and Wildman, *Chem. and Ind.*, 1955, 1159.
[4] Späth and Kahovec, *Ber.*, 1934, **67**, 1501.
[5] Kondo and Ikeda, *Ann. Report ITSUU Lab.*, 1951, **2**, 55.

the melting point of acetyldehydroisotazettinol. This and the similarity of the melting points of these two compounds would probably have led the earlier workers [5] to assume erroneously that acetyldehydroisotazettinol could not be hydrolysed with alkali. We have shown, however, by the infrared spectra that reacetylation of dehydroisotazettinol regenerated the parent compound.

Treatment of acetyldehydroisotazettinol with lithium aluminium hydride furnished isotazettatriol (V) which was characterised, after being heated with dilute sulphuric acid, as its derivative deoxyisotazettinol [1] (I; R = R″ = H, R′ = OH). Prolonged refluxing of acetyldehydroisotazettinol with sodium borohydride in methanol afforded isotazettinol [1] (I; R = H, R′ = R″ = OH) while catalytic hydrogenation of dehydroisotazettinol with platinum oxide gave rise to dihydroisotazettinol [2] (VI; R = H, R′ = R″ = OH). Whereas acetyldehydroisotazettinol was unaffected by manganese dioxide in chloroform, dehydroisotazettinol gave an αβ-unsaturated ketone, dehydrotazettinone, with the same reagent.

These results showed that dehydroisotazettinol was closely related in structure and configuration to isotazettinol.

Although acetyldehydroisotazettinol was almost neutral or so weakly basic as to be insoluble in dilute mineral acids and did not give a quaternary salt with methyl iodide, it was readily soluble in cold concentrated hydrochloric acid. When dry hydrogen chloride was passed into a chloroform–benzene solution of acetyldehydroisotazettinol, a quantitative yield of a deliquescent amorphous hydrochloride was obtained which exhibited infrared absorptions at 3330—3570 (OH and H_2O), 2500—2740 ($\equiv N^+-H$), 1620—1660 (H_2O), and 1739 cm.$^{-1}$ (OAc), but no unconjugated $>C=N^+<$ band in the region 1670—1700 cm.$^{-1}$. The hydrochloride did not give reproducible analytical values owing to high solvation, but regenerated acetyldehydroisotazettinol on basification of its aqueous solution with sodium hydrogen carbonate.

Reduction of the hydrochloride with sodium borohydride in methanol took place far more readily than in the case of the free base, and the product isolated was the known monoacetylisotazettinol [2] (I; R = H, R′ = OAc, R″ = OH) in which the acetyl group is attached to the hydroxyl allylic to the double bond in ring B of isotazettinol, as shown by conversion with manganese dioxide into the amido-lactone (IV; R = H, R′ = OAc) containing still an acetyl group.

Since the arrangement in ring B of the monoacetylisotazettinol cannot be considered to have been newly formed as a result of borohydride treatment of the hydrochloride or conversion of acetyldehydroisotazettinol into the hydrochloride, there appeared to be no doubt that acetyldehydroisotazettinol and its hydrochloride contained the same moiety as that of ring B in the monoacetylisotazettinol. Evidence in support of this was provided by the catalytic hydrogenation of the hydrochloride with palladium–carbon in water, which gave a deacetoxy-compound, demethoxytazettine [2] (I; R = R′ = H, R″ = OH), as expected.

The facts that acetyldehydroisotazettinol contains no hydroxyl group, and two hydrogen atoms less than monoacetylisotazettinol (I; R = H, R′ = OAc, R″ = OH), but is readily reduced to the latter through its hydrochloride, led us to conclude that the former compound was an epoxide, formulated as (VII; R = H, R′ = OAc), a structure which was also supported by its weak basicity.[6]

For the hydrochloride a carbinolamine structure (VIII) rather than that of an ordinary amine hydrochloride is preferable because of its highly solvated form and its ready reducibility to monoacetylisotazettinol. In support of this view, the hydrochloride readily formed an acetonyl compound [7] (X; R = H, R′ = OAc) when refluxed in acetone for a short time. Although the infrared spectrum of the hydrochloride did not indicate

[6] Bloom and Briggs, *J.*, 1952, 3591.
[7] Small and Lutz, "Chemistry of the Opium Alkaloids," U.S. Treasury Dept. Public Health Service, No. 103, 1932, p. 49.

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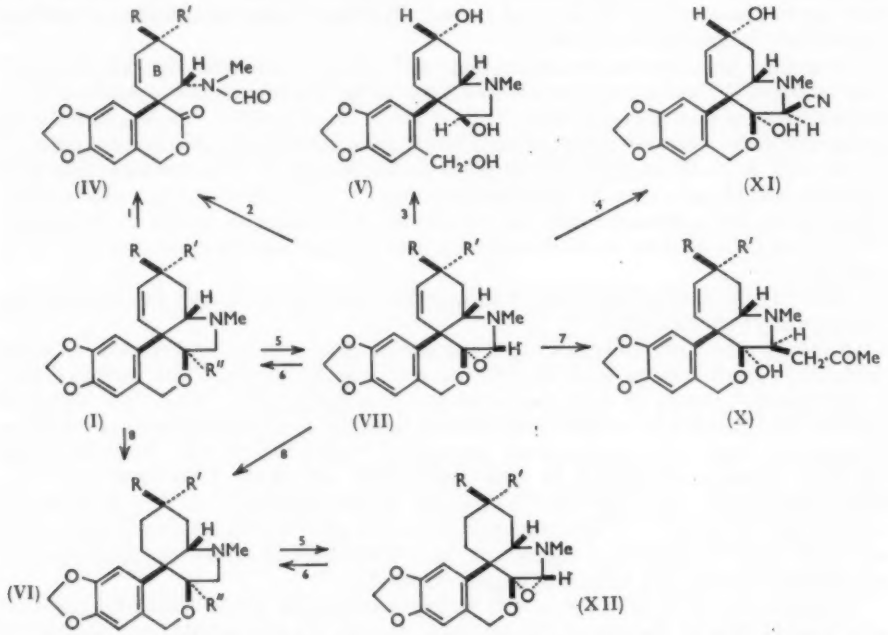
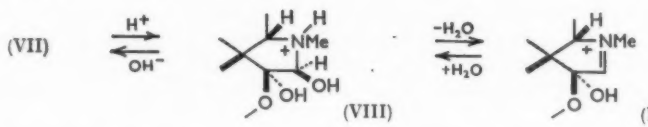
any C=N$^+$ absorption band in a solid state, it is probable that (VIII) is in equilibrium in solution with the anhydrous form (IX).



Reagents: 1, MnO_2; 2, $[Fe(CN)_6]^{3-}$–OH^-; 3, $LiAlH_4$; 4, NaCN–H^+; 5, H_2SO_4–Ac_2O; 6, H^+–$NaBH_4$ or Pd–C–H_2; 7, H^+–$COMe_2$; 8, H_2–Pt.

Dehydroisotazettinol gave likewise a hydrochloride which also gave an acetonyl compound (X; R = H, R′ = OH), acetylation of which in cold pyridine with acetic anhydride afforded a monoacetyl derivative identical with the acetonyl compound derived from acetyldehydroisotazettinol hydrochloride. Further, a reaction characteristic of



carbinolamines was observed in the formation of a cyanide (XI) when the hydrochloride was treated with sodium cyanide in boiling methanol.

With the structure of acetyldehydroisotazettinol and the hydrochloride solved, it was desirable to oxidise acetyldehydroisotazettinol (with alkaline potassium ferricyanide) to the lactam (III) The product isolated was, however, not the expected compound, but the amido-lactone (IV; R = H, R′ = OH) identical with one of the products [2] from the oxidation of isotazettinol with manganese dioxide. Presumably the lactam initially formed rearranged to the amido-lactone by a process similar to that in the manganese dioxide oxidation of tazettine mentioned above (II ⟶ III ⟶ IV).

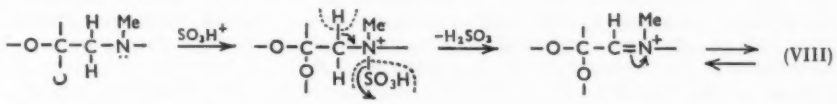
Acetyldehydrotazettinol was isomeric with acetyldehydroisotazettinol and resembled it in being almost neutral to acid and in containing one acetyl but no hydroxyl group (infrared spectrum). The hydrolysis product, dehydrotazettinol, afforded with manganese

dioxide the ketone, dehydrotazettinone (VII; R, R′ = O), obtained similarly from dehydroisotazettinol, suggesting that they were epimers in respect to the allylic hydroxyl group. Since dehydrotazettinol yielded tazettinol [1] (I; R = R″ = OH, R′ = H) on treatment of its hydrochloride with sodium borohydride, acetyldehydrotazettinol has been assigned the formula (VII; R = OAc, R′ = H) in analogy with acetyldehydroisotazettinol.

Formation of acetyldehydrotazettinol and acetyldehydroisotazettinol is considered to be the result of dehydrogenation of the intermediates, acetyltazettinol and acetylisotazettinol, derived from tazettine probably by replacement of the methoxyl group by an acetoxyl anion originating from acetic anhydride and sulphuric acid. The fact that both acetyldehydrotazettinol and acetyldehydroisotazettinol were invariably obtained when either tazettinol or isotazettinol was treated with acetic anhydride and sulphuric acid would also be accounted for by assuming that the same type of replacement took place, at least partly, during the conversion of the hydroxyl group in tazettinol or isotazettinol into the acetoxyl group.

The dehydrogenation is thought to have been caused by the sulphuric acid, acetic anhydride playing the rôle of a diluent, since the reaction mixture contained sulphurous acid as shown by a positive Malachite Green test,[8] although it was not known to us that sulphuric acid could have acted as an oxidising agent at room temperature.* In support of this, we have confirmed that other acids, such as perchloric acid and boron trifluoride, do not convert tazettine into dehydro-derivatives, the only isolable products being a mixture of diacetyltazettinol and diacetylisotazettinol.

A possible mechanism for this reaction might involve initial addition of SO_3H^+ cation to the nitrogen atom followed by elimination of the elements of sulphurous acid to give an anhydronium base, as shown.†



(VIII)

The unusual nature of the reaction prompted us to investigate other derivatives of tazettine containing the hemiketal moiety. Dihydroisotazettinol (VI; R = H, R′ = R″ = OH) gave an analogous product (XII; R = H, R′ = OAc) under the same conditions in fair yield. This acetyldehydrodihydroisotazettinol was not soluble in cold dilute mineral acids and contained one acetyl but no hydroxyl group, as shown in its infrared spectrum. Alkaline hydrolysis afforded dehydrodihydroisotazettinol (XII; R = H, R′ = OH) which gave back dihydroisotazettinol on treatment of its hydrochloride with sodium borohydride.

Dihydrotazettinol (VI; R = R″ = OH, R′ = H) similarly afforded acetyldehydrodihydrotazettinol (XII; R = OAc, R′ = H) which did not crystallise but was characterised as its saponification product, dehydrodihydrotazettinol (XII; R = OH, R′ = H). Analogous properties of the compound and reduction of its hydrochloride to dihydrotazettinol by sodium borohydride confirmed its structure.

In expectation that a methoxyl group attached to a saturated ring might be more stable than when it was allylic, an analogous reaction was carried out with dihydrotazettine (VI; R = OMe, R′ = H, R″ = OH). With the acetic anhydride–sulphuric acid complex, it gave unexpectedly a mixture from which only a small amount of acetyldehydrodihydroisotazettinol was isolated as crystals. Saponification of the mixture

* There may be some analogy between this reaction and the oxidative phosphorylation reported by Sir Alexander Todd and his collaborators (Clark, Kirby, and Todd, *Nature*, 1958, **181**, 1650).

† It is possible that the acetic anhydride formed some pyrosulphuric acid which then dissociated to yield the active species, SO_3H^+.

[8] Feigl, " Spot Tests," Elsevier Publishing Co., Amsterdam, Vol. I, 1954, p. 286.

furnished, however, both dehydrodihydroisotazettinol (XII; R = H, R′ = OH) and dehydrodihydrotazettinol (XII; R = OH, R′ = H).

Demethoxydihydrotazettine [2] (VI; R = R′ = H, R″ = OH) represents the simplest compound among those which leave the skeleton and the hemiketal moiety of tazettine unaffected, and it contains no functional groups in ring B which might be attacked by acetic anhydride and sulphuric acid. The product isolated from a neutral fraction of the reaction mixture gave analyses for $C_{17}H_{19}O_4N,\frac{1}{2}H_2O$, and showed a weak absorption at about 3333 cm.$^{-1}$ (H_2O) but no bands in the carbonyl region, indicating the absence of an acetyl group. Along with these results, the fact that its hydrochloride, prepared in benzene, reverted to demethoxydihydrotazettine (VI; R = R′ = H, R″ = OH) on treatment with either sodium borohydride or hydrogen and palladium–carbon, proved the structure of this product as dehydrodemethoxydihydrotazettine (XII; R = R′ = H).

Confirming the view that acetic anhydride–sulphuric acid complex acted upon tazettine and its derivatives as a mild oxidising agent, we have shown that dehydrodemethoxydihydrotazettine (XII; R = R′ = H) is also obtained in a low yield on oxidation of demethoxydihydrotazettine with mercuric acetate. An analogous reaction with tazettine was not successful, the only product isolated containing the metal.

Experimental

Ultraviolet absorption spectra were determined for 95% ethanol solutions, and infrared spectra for Nujol mulls unless otherwise stated. Identities were confirmed by infrared comparisons.

Acetylation of Tazettine with Acetic Anhydride and Sulphuric Acid.—(*a*) Tazettine (0·3 g.) in acetic anhydride (10 ml.) containing concentrated sulphuric acid (2 drops) was kept at about 5° for 2 days. Basification with aqueous ammonia and extraction with ether afforded a mixture (0·3 g.) which was separated by chromatography in benzene over alumina. The benzene eluate gave acetyltazettine (I; R = OMe, R′ = H, R″ = OAc) (0·17 g.), plates, m. p. and mixed m. p. 124—125° (from ethanol). Further elution with chloroform yielded unchanged tazettine (0·13 g.).

(*b*) Tazettine (0·21 g.), acetic anhydride (10 ml.), and concentrated sulphuric acid (5 drops) were kept overnight at room temperature. The mixture was poured into ice-water (60 ml.), basified with sodium hydrogen carbonate, and extracted with ether. The ethereal layer was extracted with 2% sulphuric acid, and the aqueous acidic solution basified with sodium hydrogen carbonate and extracted with ether. Evaporation of the ether gave a solid (0·15 g.), m. p. 137—140°, apparently identical with Kondo's diacetate.[5] This was chromatographed in benzene over alumina; the first benzene eluate gave diacetyltazettinol (I; R = R″ = OAc, R′ = H) (40 mg.), m. p. and mixed m. p. 199—200° (from ethanol). Further elution with benzene gave diacetylisotazettinol (I; R = H, R′ = R″ = OAc) (75 mg.), m. p. and mixed m. p. 148—150°. The ethereal layer from which the basic product had been removed as mentioned above gave, on evaporation, a solid from which acetyldehydroisotazettinol, m. p. 263° (decomp.) (10 mg.), was obtained after crystallisation from benzene. The infrared spectrum of this sample was identical with that of a sample, m. p. 254° (decomp.), previously obtained by Kondo and Ikeda.[5]

(*c*) Tazettine (1·2 g.) in acetic anhydride (10 ml.) and concentrated sulphuric acid (2 ml.) was set aside at room temperature for 2 days. The mixture was poured into ice-water, basified with sodium hydrogen carbonate, and extracted with chloroform. The water layer decolorized a dilute solution of Malachite Green. The chloroform layer was washed with 3% hydrochloric acid to remove some basic substances (0·1 g.), then washed with water, dried, and evaporated to dryness to yield a solid, which was treated with ether to separate it into a soluble and an insoluble fraction. The latter crystallised from benzene to give *acetyldehydroisotazettinol* (VII; R = H, R′ = OAc) (0·7 g.), needles, m. p. 263° (decomp.), $[\alpha]_D$ +126° (*c* 3·0 in $CHCl_3$) (lit.,[5] $[\alpha]_D$ +128·4° in $CHCl_3$), $\lambda_{max.}$ 240 and 292 mμ (log ε 3·62 and 3·57), $\nu_{max.}$ 1739 and 1724 cm.$^{-1}$ (OAc) in Nujol mull, 1724 cm.$^{-1}$ (OAc) in $CHCl_3$ (Found: C, 63·7; H, 5·1; N, 3·7; OMe, 0; *C*-Me, 4·0; Ac, 12·9. $C_{19}H_{19}NO_6$ requires C, 63·9; H, 5·4; N, 3·9; 1*C*-Me, 3·9; 1Ac, 12·0%). The former fraction was chromatographed in benzene over alumina. The first benzene eluate gave an amorphous

material (0·25 g.), and the second gave an additional crop of acetyldehydroisotazettinol (50 mg.). Re-chromatography of the above amorphous material in chloroform over silica gel and elution with chloroform gave *acetyldehydrotazettinol* (VII; R = OAc, R′ = H) (0·2 g.), m. p. 204—207° (from ligroin), $[\alpha]_D$ −26° (*c* 0·2 in $CHCl_3$), $\nu_{max.}$ 1730 cm.$^{-1}$ (OAc) (in a KBr disc) (Found: C, 64·3; H, 5·6; N, 3·5%).

Attempted Oxidation of Acetyltazettine (I; R = OMe, R′ = H, R″ = OAc), *Diacetyltazettinol* (I; R = R″ = OAc, R′ = H), *Diacetylisotazettinol* (I; R = H, R′ = R″ = OAc), *and Acetyldehydroisotazettinol* (VII; R = H, R′ = OAc) *by Manganese Dioxide.*—Acetyltazettine, diacetyltazettinol, diacetylisotazettinol, and acetyldehydroisotazettinol (0·1 g.) were severally stirred in chloroform (10—12 ml.) with manganese dioxide (1 g.) at room temperature for 24 hr. The starting materials were recovered in not less than 90% yield.

Dehydroisotazettinol.—(*a*) Acetyldehydroisotazettinol (50 mg.) was refluxed in tetrahydrofuran (10 ml.), 3% ethanolic potassium hydroxide (4 ml.), and water (2 ml.) for 1 hr. The mixture was evaporated under reduced pressure, then diluted with water, and the precipitate was collected, to give *dehydroisotazettinol* (VII; R = H, R′ = OH) (40 mg.), needles, m. p. 264° (decomp.) (from benzene), $[\alpha]_D$ +95·4° (*c* 2·4 in $CHCl_3$) $\nu_{max.}$ 3425 cm.$^{-1}$ (OH) (Found: C, 64·7; H, 5·5; N, 4·3. $C_{17}H_{17}NO_5$ requires C, 64·8; H, 5·4; N, 4·4%).

When acetyldehydroisotazettinol (50 mg.) was heated with potassium hydroxide (0·4 g.) in diethylene glycol (6 ml.) at 150° for 1 hr. 6-phenylpiperonyl alcohol (5 mg.), m. p. and mixed m. p. 101—102°, was isolated from the mixture.

(*b*) The acetate (50 mg.) in 20% hydrochloric acid (10 ml.) was heated at 100° for 10 min. Basification and extraction with chloroform afforded dehydroisotazettinol (35 mg.), m. p. 264° (decomp.), identical with the product obtained as in (*a*). Acetylation of dehydroisotazettinol with sodium acetate and acetic anhydride on a water-bath gave acetyldehydroisotazettinol (VII; R = H, R′ = OAc), m. p. 263° (decomp.).

Reduction of Acetyldehydroisotazettinol.—(*a*) Treatment of the acetate (0·12 g.) with lithium aluminium hydride (0·1 g.) in refluxing tetrahydrofuran (10 ml.) gave, in 3 hr., a triol (V) which when heated in 3% sulphuric acid (10 ml.) on a water-bath for 1 hr. afforded deoxyisotazettinol (I; R = R″ = H, R′ = OH) (0·1 g.), m. p. and mixed m. p. 120—122° (after chromatography in benzene on alumina followed by crystallisation from ether).

(*b*) Sodium borohydride (0·12 g.) was added in portions to the acetate (50 mg.) in boiling methanol (10 ml.) during 30 hr. After removal of the solvent, water was added, and the solution saturated with ammonium chloride and extracted with chloroform, to give, after concentration, isotazettinol (I; R = H, R′ = R″ = OH) (30 mg.), m. p. and mixed m. p. 204—206° (from ethanol).

Hydrogenation of Dehydroisotazettinol.—Dehydroisotazettinol (15 mg.) and platinum oxide (50 mg.) in ethanol (10 ml.) were stirred in hydrogen at room temperature. After 6 hr. the mixture was filtered and evaporated to dryness, and the residue taken up into chloroform and extracted with 3% hydrochloric acid. The acidic layer afforded, after basification and extraction with chloroform, dihydroisotazettinol (VI; R = H, R′ = R″ = OH), m. p. and mixed m. p. 250°.

Oxidation of Dehydroisotazettinol by Manganese Dioxide.—Dehydroisotazettinol (60 mg.) in chloroform (8 ml.) was stirred with manganese dioxide (0·7 g.) at room temperature for 22 hr. The product isolated with chloroform gave *dehydrotazettinone* (VII; R, R′ = O), needles, m. p. 271° (decomp.) (from acetone), $\nu_{max.}$ 1684 cm.$^{-1}$ (conjugated ketone) (Found: C, 61·9; H, 5·4. $C_{17}H_{15}NO_5,H_2O$ requires C, 61·6; H, 5·2%).

Acetyldehydroisotazettinol Hydrochloride.—Dry hydrogen chloride was passed into a solution of acetyldehydroisotazettinol (0·1 g.) in chloroform (1 ml.) and benzene (20 ml.) with cooling. This gave the hydrochloride (0·1 g.) as a white deliquescent powder, which was washed with benzene, then with light petroleum (b. p. 60—80°), and dried over P_2O_5 *in vacuo*. An aqueous solution of the hydrochloride regenerated acetyldehydroisotazettinol on neutralisation with sodium hydrogen carbonate.

Hydrogenation of the hydrochloride (90 mg.) in water (20 ml.) with 5% palladium–carbon (0·1 g.) at room temperature for 1·5 hr. gave demethoxytazettine (I; R = R′ = H, R″ = OH) (70 mg.), m. p. and mixed m. p. 193—194° (from ether).

The hydrochloride (0·1 g.) dissolved in boiling acetone (10 ml.) in a few minutes. After 1 hr., the mixture was evaporated to give a residue which was taken up in water, washed with chloroform, basified with sodium carbonate, and extracted with chloroform. Concentration

of the chloroform extract yielded the *acetonyl derivative* (X; R = H, R′ = OAc), m. p. 156—157°, prisms from methanol, $[\alpha]_D$ +250° (*c* 0·96 in $CHCl_3$), $\nu_{max.}$ 3289 (OH) and 1720 cm.$^{-1}$ (CO, OAc) (Found: C, 63·9; H, 6·1. $C_{22}H_{25}NO_7$ requires C, 63·6; H, 6·1%).

Sodium borohydride (0·15 g.) in methanol (10 ml.) was added dropwise to a stirred solution of the foregoing hydrochloride (80 mg.) in methanol (20 ml.) at 5°. After 1 hr., the mixture was acidified with acetic acid and evaporated to dryness; the residue was redissolved in water and basified with aqueous ammonia. Extraction with ether and evaporation of the extract afforded monoacetylisotazettinol (I; R = H, R′ = OAc, R″ = OH) (50 mg.), m. p. and mixed m. p. 193—194° (from ethanol).

Oxidation of Monoacetylisotazettinol by Manganese Dioxide.—Acetylisotazettinol (35 mg.) in chloroform (8 ml.) was stirred with manganese dioxide (0·5 g.) for 26 hr. The oxide was filtered off and washed with chloroform, and the combined filtrate and washings were evaporated to give the *amido-acetate* (IV; R = H, R′ = OAc), leaflets (from methanol), m. p. 266—267°, $\nu_{max.}$ 1736 (OAc), 1718 (lactone), and 1672 cm.$^{-1}$ (amide) in Nujol mull, and 1737 (OAc), 1724 (lactone), and 1675 cm.$^{-1}$ (amide) in $CHCl_3$ (Found: C, 61·5; H, 5·0. $C_{19}H_{19}NO_7$ requires C, 61·1; H, 5·1%). Hydrolysis of this (5 mg.) by 1% methanolic potassium hydroxide on a water-bath for 3 min., followed by acidification with dilute hydrochloric acid, gave the amide (IV; R = H, R′ = OH) (2 mg.), m. p. and mixed m. p. 207—209°. Reacetylation of the latter with acetic anhydride in pyridine gave the foregoing amido-acetate (IV; R = H, R′ = OAc).

Dehydroisotazettinol Hydrochloride.—The hydrochloride was obtained as a deliquescent white powder by the procedure described for acetyldehydroisotazettinol hydrochloride. The infrared spectrum of this showed absorptions at 3200 (OH), 2740—2500 (≡N$^+$H) and 1626 cm.$^{-1}$ (H_2O). The hydrochloride regenerated the dehydro-base (VII; R = H, R′ = OH) on neutralisation of its aqueous solution with sodium hydrogen carbonate.

An aqueous solution (20 ml.) of the hydrochloride (50 mg.) was hydrogenated over 5% palladium–carbon (0·1 g.) for 4 hr. Removal of the catalyst followed by basification of the filtrate and extraction with chloroform gave isotazettinol (I; R = H, R′ = R″ = OH) (24 mg.), m. p. and mixed m. p. 204—206° (from ethanol).

The above hydrochloride was heated under reflux in acetone for 2 hr., during which it gradually changed to colourless prisms. The resulting *acetonyl derivative hydrochloride* was crystallised from acetone, to give prisms, m. p. 187—188° (decomp.), $\nu_{max.}$ 3330—3030 (OH), 2700—2500 (≡N$^+$H), 1706 (CO), and 1640—1620 cm.$^{-1}$ (H_2O) (Found: C, 58·7; H, 6·5. $C_{20}H_{23}NO_6$,HCl requires C, 58·9; H, 5·9%). The hydrochloride thus obtained was dissolved in water, basified with sodium carbonate, and extracted with chloroform. Concentration of the chloroform solution yielded the *acetonyl derivative* (X; R = H, R′ = OH), m. p. 180—181°, prisms from methanol, $[\alpha]_D$ +193° (*c* 0·97 in $CHCl_3$), $\nu_{max.}$ 3185 (OH) and 1712 cm.$^{-1}$ (CO) (Found: C, 64·4; H, 6·2. $C_{20}H_{23}NO_6$ requires C, 64·3; H, 6·2%). Acetylation of this (30 mg.) with acetic anhydride (0·5 ml.) and pyridine (1 ml.) at room temperature overnight gave the acetate (X; R = H, R′ = OAc), m. p. 156—157°, identical with the acetonyl compound derived from acetyldehydroisotazettinol.

The hydrochloride (100 mg.) and sodium cyanide (200 mg.) in methanol (10 ml.) were heated under reflux for 3 hr. The precipitated sodium chloride was filtered off and the filtrate was evaporated to dryness, to give a residue which was extracted with chloroform. The extract was washed with water, dried, and evaporated, affording the *cyano-compound* (XI) (50 mg.) as colourless needles, m. p. 225—227° (decomp.) (from ethanol), $\nu_{max.}$ 3257 (OH) and 2232 cm.$^{-1}$ (CN) (Found: C, 63·0; H, 5·4; N, 8·1. $C_{18}H_{18}N_2O_5$ requires C, 63·2; H, 5·3; N, 8·2%).

Ferricyanide Oxidation of Acetyldehydroisotazettinol.—Potassium ferricyanide (0·5 g.) and potassium hydroxide (0·3 g.) in water (10 ml.) were added to acetyldehydroisotazettinol (VII; R = H, R′ = OAc) (70 mg.) in hot dioxan (10 ml.), and the mixture was heated on a water-bath for 1 hr. After dilution with water, the mixture was washed with chloroform, acidified with dilute sulphuric acid, and extracted with chloroform. Concentration of the extract gave the amide (IV; R = H, R′ = OH) (5 mg.), m. p. and mixed m. p. 216—218° after crystallisation from methanol and drying over P_2O_5.

Dehydrotazettinol.—Acetyldehydrotazettinol (VII; R = OAc, R′ = H) (50 mg.) was refluxed in 3% ethanolic potassium hydroxide (10 ml.) for 1 hr. The mixture was concentrated to half-volume, diluted with water, and extracted with chloroform, to give *dehydrotazettinol* (VII; R = OH, R′ = H) (32 mg.), prisms, m. p. 244—245° (decomp.) (from benzene), $[\alpha]_D$

XUM

+28° (*c* 0·7 in $CHCl_3$), $\nu_{max.}$ 3213 cm.$^{-1}$ (OH) (Found: C, 67·3; H, 5·7. $C_{17}H_{17}NO_5,\frac{1}{2}C_6H_6$ requires C, 67·8; H, 5·7%).

Oxidation of Dehydrotazettinol by Manganese Dioxide.—Dehydrotazettinol (25 mg.) in chloroform (10 ml.) was stirred with manganese dioxide (0·5 g.) at room temperature for 1 hr. After removal of the manganese dioxide and concentration of the filtrate to dryness, the residue was crystallised from acetone to furnish dehydrotazettinone (VII; R, R′ = O), m. p. and mixed m. p. 271° (decomp.).

Reduction of Dehydrotazettinol Hydrochloride by Sodium Borohydride.—Dehydrotazettinol (20 mg.) was dissolved in methanol (2 ml.) containing concentrated hydrochloric acid (2 drops), then evaporated to dryness, and the resulting hydrochloride, redissolved in methanol (2 ml.), was treated with sodium borohydride (0·1 g.) at room temperature for 1 hr. The mixture was concentrated and taken up into water which was saturated with ammonium chloride and extracted with chloroform. The chloroform extract was dried and evaporated, to yield tazettinol (I; R = R″ = OH, R′ = H) (15 mg.), m. p. and mixed m. p. 185—187°.

Conversion of Tazettinol or Isotazettinol into Dehydrotazettinol and Dehydroisotazettinol.—(*a*) Tazettinol (I; R = R″ = OH, R′ = H) (100 mg.) in acetic anhydride (5 ml.) and concentrated sulphuric acid (1 ml.) was kept overnight at room temperature. The mixture was poured into ice-water, basified with sodium hydrogen carbonate, and extracted with chloroform. The chloroform extract was washed with 3% hydrochloric acid, dried, and evaporated to dryness and the residue hydrolysed in 10% methanolic potassium carbonate (20 ml.) under reflux for 3 hr. After removal of methanol, water was added and the whole extracted with chloroform. Concentration of the chloroform gave a gum which was chromatographed in benzene over alumina. The benzene eluate gave dehydroisotazettinol (VII; R = H, R′ = OH) (40 mg.), m. p. 262—263° (decomp.); elution with acetone gave dehydrotazettinol (VII; R = OH, R′ = H) (30 mg.), m. p. 238—241° (decomp.).

(*b*) Isotazettinol (I; R = H, R′ = R″ = OH) (110 mg.) was treated with acetic anhydride (5 ml.) and concentrated sulphuric acid (1 ml.) for 12 hr. at room temperature and worked up as described in (*a*), whereupon there were obtained dehydroisotazettinol (VII; R = H, R′ = OH) (55 mg.) and dehydrotazettinol (VII; R = OH, R′ = H) (10 mg.).

Action of Acetic Anhydride and Boron Trifluoride on Tazettine.—Tazettine (280 mg.) in acetic anhydride (5 ml.) and boron trifluoride–ether complex (1·5 ml.) was set aside for 12 hr. The mixture was poured into water (50 ml.) and basified with sodium carbonate, and the deposited precipitate collected, washed with water, dried (290 mg.; m. p. 139—142°), and crystallised from ether, to give diacetylisotazettinol (I; R = H, R′ = R″ = OAc) (180 mg.), m. p. and mixed m. p. 148—150°. The mother-liquor from this was dissolved in ether and extracted with 3% hydrochloric acid. Basification and extraction of the acidic solution yielded an oil which was chromatographed in benzene over alumina. From the first benzene eluate, diacetyltazettinol (I; R = R″ = OAc, R′ = H) (40 mg.), m. p. and mixed m. p. 199—200°, was isolated and the second benzene eluate yielded an additional crop of diacetylisotazettinol (10 mg.). The ethereal extract gave only a trace of gum, no dehydro-base being isolated.

Action of Acetic Anhydride and Perchloric Acid on Tazettine.—60% Perchloric acid (20 drops) was added dropwise with cooling to tazettine (0·2 g.) in acetic anhydride (5 ml.), and the whole kept at 10° for 24 hr. The mixture was poured into water (50 ml.), filtered, basified with sodium carbonate, and extracted with chloroform, and the chloroform solution was extracted with 1% hydrochloric acid. Basification of the aqueous layer and extraction with ether furnished diacetylisotazettinol (100 mg.), m. p. and mixed m. p. 141—144°. The chloroform layer gave, on concentration, diacetyltazettinol (100 mg.), m. p. and mixed m. p. 199—200°. No neutral substances were isolated from the reaction mixture.

Action of Sulphuric Acid and Acetic Anhydride on Dihydroisotazettinol.—Dihydroisotazettinol (VI; R = H, R′ = R″ = OH) (130 mg.) in acetic anhydride (5 ml.) containing concentrated sulphuric acid (0·5 ml.) was kept at room temperature overnight and worked up as described above. The *acetyldehydrodihydroisotazettinol* (XII; R = H, R′ = OAc) (90 mg.) thus obtained crystallised from chloroform–ethanol as needles, m. p. 240—241°. The infrared spectrum showed a band at 1721 cm.$^{-1}$ (OAc) but no absorptions in the 3 μ region (Found: C, 63·8; H, 6·0. $C_{19}H_{21}NO_6$ requires C, 63·5; H, 5·9%).

Dehydrodihydroisotazettinol.—Acetyldehydrodihydroisotazettinol (50 mg.) in tetrahydrofuran (10 ml.) and 3% methanolic sodium hydroxide (5 ml.) was heated on a water-bath

for 2 hr. After evaporation of the mixture, water was added and the precipitate formed was collected, washed with water and methanol, and crystallised from methanol, to give *dehydrodihydroisotazettinol* (XII; R = H, R′ = OH) as prisms, m. p. 252° (decomp.), $[\alpha]_D$ −77° (*c* 1·06 in $CHCl_3$), $\nu_{max.}$ 3378 cm.$^{-1}$ (OH) (Found: C, 64·6; H, 6·1. $C_{17}H_{19}NO_5$ requires C, 64·3; H, 6·0%). The m. p. was depressed to 230—240° on admixture with dihydroisotazettinol, m. p. 250°.

The hydrochloride, prepared as described above, crystallised from methanol–ether as white needles which showed no distinct m. p., gradually becoming brown at 180—190°; they had $\nu_{max.}$ 3436, 3257 (OH), 2750—2550 (≡N$^+$H), and 1620 cm.$^{-1}$ (H_2O). This salt regenerated the base (XII; R = H, R′ = OH) on basification of its aqueous solution; extraction with chloroform gave this base.

The hydrochloride (20 mg.) in methanol (3 ml.) was stirred with sodium borohydride (50 mg.) for 1 hr. at room temperature. Working up as usual afforded dihydroisotazettinol (VI; R = H, R′ = R″ = OH), m. p. and mixed m. p. 246—248° (prisms from ethanol), in good yield.

Dihydrotazettinol.—Tazettinol (100 mg.) in ethanol (10 ml.) was hydrogenated in the presence of platinum oxide (100 mg.) for 5 hr. at room temperature. The mixture was filtered and evaporated, to give *dihydrotazettinol* (VI; R = R″ = OH, R′ = H) (100 mg.) as prisms, m. p. 218—220° (from ethanol), $\nu_{max.}$ 3300 and 3155 cm.$^{-1}$ (OH) (Found: C, 64·3; H, 6·6. $C_{17}H_{21}NO_5$ requires C, 63·9; H, 6·6%).

Dehydrodihydrotazettinol.—Dihydrotazettinol (50 mg.) was treated with acetic anhydride (3 ml.) and concentrated sulphuric acid (0·2 ml.) at room temperature overnight and the mixture worked up in the usual manner, to give acetyldehydrodihydrotazettinol (XII; R = OAc, R′ = H) which failed to crystallise. The product showed an infrared absorption at 1727 cm.$^{-1}$ (OAc). Hydrolysis of it in 5% ethanolic sodium hydroxide (10 ml.) under reflux for 2 hr. gave *dehydrodihydrotazettinol* (XII; R = OH, R′ = H) (15 mg.), m. p. 220—221° (from benzene), $[\alpha]_D$ −119° (*c* 0·32 in $CHCl_3$), $\nu_{max.}$ 3413 cm.$^{-1}$ (OH) (Found: C, 64·6; H, 6·1. $C_{17}H_{19}NO_5$ requires C, 64·3; H, 6·0%). The m. p. was depressed to 180—190° on admixture with dihydrotazettinol, m. p. 218—220°.

Dehydrodihydrotazettinol (50 mg.) was converted into its hydrochloride by adding concentrated hydrochloric acid to its methanolic solution and evaporating the mixture under reduced pressure. The hydrochloride thus obtained was treated with sodium borohydride (100 mg.) in methanol (2 ml.) for 1 hr. at room temperature; this yielded dihydrotazettinol (VI; R = R″ = OH, R′ = H) (35 mg.), m. p. and mixed m. p. 218—220°.

Action of Sulphuric Acid and Acetic Anhydride on Dihydrotazettine.—Dihydrotazettine (VI; R = OMe, R′ = H, R″ = OH) (0·3 g.) in acetic anhydride (5 ml.) and concentrated sulphuric acid (1 ml.) was kept for 24 hr. at room temperature. The mixture was poured into ice-water, basified with sodium hydrogen carbonate, and extracted with chloroform. The chloroform extracts were concentrated to give a gum (0·25 g.) which was chromatographed in chloroform over silica gel. The chloroform eluate gave a colourless gum which, when triturated with ethanol, gave a small quantity of acetyldehydrodihydroisotazettinol (XII; R = H, R′ = OAc), m. p. and mixed m. p. 241—242°. The mother-liquor was hydrolysed in 3% ethanolic sodium hydroxide (10 ml.), and the product (0·17 g.) was chromatographed in benzene over alumina. The first benzene eluate gave a gum (30 mg.); further elution with benzene and benzene–chloroform (1 : 1) gave dehydrodihydroisotazettinol (XII; R = H, R′ = OH) (40 mg.), m. p. and mixed m. p. 252° (decomp.), and with chloroform and chloroform–acetone (2 : 1) gave dehydrodihydrotazettinol (XII; R = OH, R′ = H) (60 mg.), m. p. and mixed m. p. 219—221°.

Action of Sulphuric Acid and Acetic Anhydride on Demethoxydihydrotazettine.—Concentrated sulphuric acid (0·5 ml.) was added to demethoxydihydrotazettine (VI; R = R′ = H, R″ = OH) (150 mg.) in acetic anhydride (5 ml.). After being kept at room temperature for 12 hr. the mixture was poured into water (20 ml.), basified with sodium hydrogen carbonate, and extracted with chloroform (2 × 20 ml.). The aqueous layer gave a positive Malachite Green test for sulphurous acid. The dried chloroform extracts were concentrated to dryness and the residue was extracted with cold 5% hydrochloric acid and benzene. The organic layer was dried and evaporated, to yield *dehydrodemethoxydihydrotazettine* XII; R = R′ = H) (90 mg.), prisms (from ethanol), m. p. 260° (decomp.), $[\alpha]_D$ −46° (*c* 1·34 in $CHCl_3$) (Found: C, 65·8; H, 6·5. $C_{17}H_{19}NO_4,\frac{1}{2}H_2O$ requires C, 65·8; H, 6·5%). The infrared spectrum showed very weak band at 3·0 μ (water of crystallisation) but no absorptions in the 5 μ region.

XUM

Dehydrodemethoxydihydrotazettine Hydrochloride.—Dry hydrogen chloride was passed into a solution of the dehydro-base (0·1 g.) in benzene (10 ml.). The precipitated hydrochloride was collected, washed repeatedly with benzene and ether, and dried over P_2O_5, to give a hygroscopic white powder, $\nu_{max.}$ 3333 and 3125 (OH and H_2O), 2740—2500 ($\equiv N^+H$), and 1626 cm.$^{-1}$ (H_2O). Basification of an aqueous solution of the hydrochloride and extraction with chloroform regenerated the base (XII; R = R′ = H).

The hydrochloride (50 mg.) and excess of sodium borohydride in methanol (10 ml.) were stirred at room temperature for 1 hr. The mixture was acidified with 5% hydrochloric acid, then evaporated to dryness; the residue was redissolved in water, washed with ether, basified with sodium carbonate, and extracted with chloroform, to afford demethoxydihydrotazettine (VI; R = R′ = H, R″ = OH), m. p. and mixed m. p. 164—166° (from ethanol), in nearly quantitative yield.

The hydrochloride (20 mg.) in 2% hydrochloric acid (10 ml.) was hydrogenated over 10% palladium–carbon (100 mg.) for 2 hr. at room temperature. After working up in the usual manner, the mixture gave demethoxydihydrotazettine (VI; R = R′ = H, R″ = OH), m. p. and mixed m. p. 164—166°.

Oxidation of Demethoxydihydrotazettine by Mercuric Acetate.—Demethoxydihydrotazettine (VI; R = R′ = H, R″ = OH) (120 mg.) and mercuric acetate (150 mg.) in 10% acetic acid (5 ml.) were heated on a water-bath for 40 min. The precipitated mercurous acetate was removed and the filtrate saturated with hydrogen sulphide and again filtered. The filtrate was basified with sodium carbonate and extracted with chloroform, which was washed with 5% hydrochloric acid to remove some unchanged starting material (50 mg.). Concentration of the washed chloroform solution gave a gum (40 mg.) which was chromatographed in benzene over neutral alumina. A benzene eluate gave the dehydro-compound (XII; R = R′ = H) (10 mg.) (prisms from ethanol), m. p. and mixed m. p. 260—261° (decomp.). A methanol eluate gave a gum (25 mg.) which was not investigated.

Oxidation of Tazettine with Mercuric Acetate.—Tazettine (200 mg.) and mercuric acetate (400 mg.) in 10% acetic acid (5 ml.) were heated on a water-bath for 10 min. The mercurous acetate which was deposited was removed and the filtrate saturated with hydrogen sulphide, to give mercury sulphide which was removed with the aid of Filter-Cel. The filtrate was basified with aqueous sodium hydroxide and extracted with chloroform. The chloroform was washed with 5% hydrochloric acid to remove some unchanged starting material (50 mg.) and then concentrated to dryness, giving a gum (100 mg.). This was chromatographed in benzene over alumina. A benzene eluate gave a trace of gum; elution with chloroform afforded a solid (60 mg.) which was rechromatographed in chloroform over silica gel. The first eluate therefrom gave a white substance (50 mg.) which crystallised from ethanol as fine needles, m. p. 226—228° (decomp.), $\lambda_{max.}$ 290 mμ, $\nu_{max.}$ 3571—3448 (OH) and 1739 cm.$^{-1}$ (CO) (Found: C, 37·8; H, 3·9; N, 2·6%). This was very soluble in chloroform, benzene, and acetone, sparingly in ethanol, methanol, and ether, and contained mercury.

We are indebted to Dr. W. I. Taylor, CIBA Pharmaceutical Products, Inc., Summit, New Jersey, U.S.A., Dr. W. C. Wildman, National Heart Institute, National Institutes of Health, Bethesda, Md., U.S.A., and Professor Y. Yukawa, Institute of Scientific and Industrial Research, Osaka University, for valuable discussions, and to the Ministry of Education (Japan) for a grant from the Research Fund.

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[*Received, August 15th,* 1960.]

214. *Reactions of Nitriles. Part I. Condensation of Methyleneaminoacetonitrile with Aldehydes.*

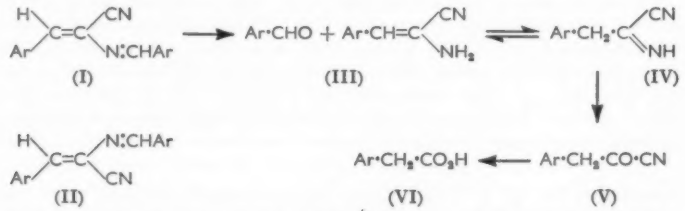
By (Miss) D. D. Vaghani and J. R. Merchant.

The preparation of a number of 2-cyanostyrene derivatives by the condensation of methyleneaminoacetonitrile with aromatic aldehydes is described. In alkali or acids the styrenes yield phenylacetic acids or imidazole derivatives.

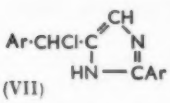
Mahajani and Ray [1] report that methyleneaminoacetonitrile reacts with aldehydes to form unsaturated nitriles which on reduction give amino-acids, *e.g.*, with formaldehyde and acetaldehyde it yields DL-serine and DL-threonine respectively.[1,2]

With the object of preparing substituted phenylalanines we caused various aromatic aldehydes to react with methyleneaminoacetonitrile in presence of sodium ethoxide. Numerous other basic catalysts failed to cause condensation, as did dry hydrogen chloride (except that for veratraldehyde piperidine could be used); and of the aldehydes tried many gave only the derived acids or indefinite products.

p-Anisaldehyde gave *p*-anisic acid and two crystalline isomers that are assigned structures (I) and (II) on the basis of analyses and the following infrared bands, common to both of them: 4·56 (C≡N); 6·19, 6·27 (C=C–Ar); 6·42 μ (C=N). Of the two, the higher-melting is assigned the *trans*-structure (H and CN at the C=C linkage) (II) because of its ultraviolet absorption (in ethanol) at 242, 283, 360, and 375 mμ (log ε 4·15, 4·43, 4·49, 4·5), the isomer having maxima at 240, 285, and 360 mμ (log ε 2·11, 1·99, 2·7), and because the low-melting gave the high-melting form when its hydrochloride was heated in nitrobenzene. Six other aldehydes gave similar products, but only three of these were obtained in both forms. The same products were obtained by condensation with aminoacetonitrile in place of methyleneaminoacetonitrile, and the original reaction doubtless involved hydrolysis of the latter reagent to the former and condensation of the aminoacetonitrile with two mols. of aldehyde.



Heating the product (II; Ar = *p*-MeO·C_6H_4) with aqueous acid or alkali gave *p*-methoxyphenylacetic acid, presumably by the steps (III)—(VI). Hydrolysis with alcoholic alkali gave the same acid (VI) with a very small amount of the acid Ar·CH=C(CO_2H)·N:CHAr. Hydrolysis with alcoholic hydrochloric acid gave the acid (VI) and a compound, $C_{18}H_{17}ClN_2O_2$, that gave a picrate and was recovered unchanged on treatment with boiling acid or alkali. From this stability and from infrared bands at 3 (NH), 6·53 (C=N), 8·07, 8·55, and 9·76 (OMe), and 6·34, 6·64, and 12 μ (arene), and absence of a C≡N band, this product is assigned the imidazole structure (VII). Most of the other products of types (I) and (II) gave similar products on treatment with aqueous or alcoholic acid. Formation of imidazoles from anilinoacetonitrile and aldehydes has been reported by Minovici.[3]



(VII)

[1] Mahajani and Ray, *J. Indian Chem. Soc.*, 1956, **33**, 455.
[2] Guha and Ray, *J. Indian Chem. Soc.*, 1958, **35**, 695.
[3] Minovici, *Ber.*, 1896, **29**, 2097.

Experimental

Condensation of Aldehydes with Methyleneaminoacetonitrile.—A boiling suspension of the nitrile (0·05 mole) in absolute ethanol (60 c.c.) was mixed with a boiling solution of the aldehyde (0·05 mole) in ethanol (30 c.c.). The mixture was allowed to cool to 44° and sodium ethoxide (0·05 mole) in ethanol (57·5 c.c.) was added in portions with shaking. The mixture was kept at 48° for 24 hr. A small amount of unchanged nitrile was removed and the solution acidified with acetic acid. The colourless precipitate of arenecarboxylic acid was collected. The alcoholic filtrate, on concentration to less than half its volume and cooling, deposited the yellow cis(H/CN)-*α-arylideneaminocinnamonitrile* (I) that was collected, washed with alcohol and water, and recrystallised from alcohol or benzene (yield 0·6—0·8 g.). In some cases small amounts of the trans-*isomer* was deposited when the mother-liquor was kept for 4—5 days. The *products* are recorded in Table 1.

Table 1. *Substituted α-arylideneaminocinnamonitriles* (I, II).

			Found (%)				Required (%)		
Subst.	Form *	M. p.	C	H	N	Formula	C	H	N
p-MeO	*cis*	130°	73·9	5·2	9·4	$C_{18}H_{16}N_2O_2$	74·0	5·4	9·6
	trans	142	74·0	5·6	9·3				
p-EtO	*cis*	108	—	—	8·8	$C_{20}H_{20}N_2O_2$	75·0	6·3	8·7
	trans	140	74·9	6·3	8·6				
p-Ph·CH_2·O	*cis*	148	81·3	5·3	6·6	$C_{30}H_{24}N_2O_2$	81·1	5·4	6·3
p-NMe_2	*cis*	223	75·5	6·8	17·9	$C_{20}H_{22}N_4$	75·5	6·9	17·6
3,4-CH_2O_2	*cis*	218	67·4	3·4	8·9	$C_{18}H_{12}N_2O_4$	67·5	3·7	8·8
3,4-$(MeO)_2$	*cis*	172	68·0	6·0	7·7	$C_{20}H_{20}N_2O_4$	68·2	5·7	8·0
	trans	178	68·3	6·0	8·3				
2,4-$(MeO)_2$	*cis*	159	67·9	5·4	8·3	$C_{20}H_{20}N_2O_4$	68·2	5·7	8·0
	trans	170	68·0	5·4	8·1				

Reagents found unsuccessful were piperidine (except for veratraldehyde), diethylamine, sodium methoxide and butoxide, potassium carbonate, sodium acetate and hydroxide, and hydrogen chloride.

When sodium ethoxide was used, benzaldehyde, *p*-tolualdehyde, *p*-chloro- and *p*-methoxybenzaldehyde, and 2-formylthiophen gave only the corresponding acids; *p*-nitro- and *p*-hydroxy-benzaldehyde and protocatechualdehyde gave indefinite products.

Condensation of Aldehydes with Aminoacetonitrile.—A boiling suspension of aminoacetonitrile hydrogen sulphate (0·025 mole) in absolute alcohol (30 c.c.) and a solution of an aldehyde (0·025 mole) in boiling alcohol (15 c.c.) were mixed. Sodium ethoxide (0·05 mole) in alcohol (57·5 c.c.) was added to the mixture at 44°, and the whole was kept at room temperature for 24 hr. This gave the *cis*-isomer of the arylideneaminocinnamonitrile. In the case of 2,4-dimethoxybenzaldehyde, the *trans*-isomer was also obtained in very small amount, after concentration of the mother-liquor at reduced pressure.

Treatment of the Cinnamonitriles with Aqueous Hydrochloric Acid.—The nitrile was heated

Table 2. *Substituted phenylacetic acids.*

		Found (%)			Calc. (%)	
Subst.	M. p.	C	H	Formula	C	H
p-MeO	84°	65·1	5·9	$C_9H_{10}O_3$	65·1	6·0
p-EtO	83	66·8	6·8	$C_{10}H_{12}O_3$	66·6	6·6
p-Ph·CH_2·O	120	74·3	5·4	$C_{15}H_{14}O_3$	74·4	5·7
3,4-CH_2O_2	123	60·3	4·7	$C_9H_8O_4$	60·0	4·4
3,4-$(MeO)_2$	96	61·1	6·2	$C_{10}H_{12}O_4$	61·2	6·1
2,4-$(MeO)_2$	107	61·4	6·4	$C_{10}H_{12}O_4$	61·2	6·1

on a steam-bath with 15% hydrochloric acid (40 c.c. per g.) with shaking; the nitrile dissolved and an oil separated. The cooled mixture was extracted repeatedly with ether. The combined extracts were extracted with sodium hydrogen carbonate solution. This carbonate extract was acidified with hydrochloric acid, yielding the arylacetic acid which was recovered

by means of ether, sublimed or recrystallised and identified by a mixed m. p. determination. The acids thus obtained are recorded in Table 2.

On evaporation the original ether layer afforded a brown oil that gave the 2,4-dinitrophenylhydrazone of the corresponding aldehyde.

Hydrolysis with concentrated hydrochloric acid and dilute sulphuric acid gave the same result.

Hydrolysis of the Cinnamonitriles with Alcoholic Hydrochloric Acid.—The nitrile (I; Ar = *p*-MeO·C_6H_4) (2 g.) was refluxed for 2 hr. with alcohol (125 c.c.) which had been saturated with dry hydrogen chloride at 0°. The solution was then distilled at reduced pressure. The residual brown syrup, on cooling, gave the crystalline 3-(α-*chloro*-4-*methoxybenzyl*)-2-p-*methoxyphenylimidazole* (0·55 g.). When washed with a little acetone and repeatedly crystallised from dilute alcohol it formed needles, m. p. 184° (Found: C, 65·9; H, 5·4; N, 8·8; Cl, 10–6; OMe, 18·9. $C_{18}H_{17}ClN_2O_2$ requires C, 65·8; H, 5·1; N, 8·5; Cl, 10·8; 2OMe, 18·9%).

The acetone solution, on evaporation under reduced pressure, left a residue which was taken up in ether (insoluble part was rejected). The ether layer was washed successively with dilute hydrochloric acid, water, and aqueous sodium hydrogen carbonate. The carbonate extract, on acidification with dilute hydrochloric acid, afforded *p*-methoxyphenylacetic acid, m. p. and mixed m. p. 83° (from water), that was isolated by means of ether.

The ethoxy-analogue (I; Ar = *p*-EtO·C_6H_4) gave the analogous *imidazole*, m. p. 187° (Found: C, 67·3; H, 6·2; N, 8·3. $C_{20}H_{21}ClN_2O_2$ requires C, 67·4; H, 5·9; N, 7·9%).

The nitrile (I; R = 3,4-CH_2O_2:C_6H_3) (2 g.) from piperonaldehyde was refluxed with alcoholic hydrochloric acid (150 c.c., prepared as above) for 3 hr. The precipitated ammonium chloride was filtered off and the alcohol removed under reduced pressure, giving a mixture of brown oil and ammonium chloride. This was treated with ether and dilute hydrochloric acid, a brown mass remaining insoluble. This mass was washed with acetone and the residue was crystallised repeatedly from dilute alcohol to give the *imidazole*, m. p. 183° (0·070 g.) (Found: N, 7·8; Cl, 9·5. $C_{18}H_{13}ClN_2O_4$ requires N, 7·8; Cl, 9·8%). Homopiperonylic acid was obtained from the ether-soluble part, by working up as above.

The nitrile [I; Ar = 3,4-$(MeO)_2C_6H_3$] (4 g.) was refluxed with alcoholic hydrochloric acid (300 c.c.) for 2 hr. An orange insoluble *hydrochloride* of the nitrile was then filtered off, washed with alcohol, and crystallised from dioxan in needles, m. p. 200° (2·4 g.) (Found: N, 7·7; Cl, 8·7. $C_{20}H_{21}ClN_2O_4$ requires N, 7·5; Cl, 9·1%). When crystallised from boiling nitrobenzene this hydrochloride yielded the basic trans-*nitrile*, which was isolated from the solution by precipitation with light petroleum and crystallised from benzene in needles, m. p. 178° (Found: C, 68·3; H, 6·0; N, 8·2. $C_{20}H_{20}N_2O_4$ requires C, 68·2; H, 5·7; N, 7·9%). The original alcoholic filtrate was evaporated under reduced pressure, giving a residue which was treated with a little acetone; ammonium chloride separated and was filtered off. Removal of acetone from the filtrate yielded a brown mass which on treatment with ether and dilute hydrochloric acid gave the *hydrochloride* of an imidazole (124 mg.). Crystallised from alcohol, this had m. p. 235° (decomp.) (Found: C, 57·0; H, 5·5; N, 6·5; Cl, 16·1. $C_{20}H_{22}Cl_2N_2O_4$ requires C, 56·6; H, 5·2; N, 6·6; Cl, 16·5%). On working up the ether-soluble part, as described above, it gave a brown mass whence sublimation afforded homoveratric acid.

Hydrolysis of the Cinnamonitriles with Alcoholic Alkali.—The nitrile (I; Ar = *p*-MeO·C_6H_4) (1 g.) was boiled under reflux with alcoholic sodium hydroxide (1 g. in 94 c.c. of 70% alcohol) for 16 hr. The solvent was distilled off at reduced pressure and the residue treated with water and extracted with ether. The ether layer was washed, dried (Na_2SO_4), and distilled to give a brown oil (0·22 g.) which gave anisaldehyde 2,4 dinitrophenylhydrazone. The aqueous layer was acidified with hydrochloric acid and extracted with ether. The ether layer was washed, dried, and evaporated. The residue, on treatment with benzene, afforded 4-*methoxy*-α-(p-*methoxybenzylideneamino*)*cinnamic acid* (0·050 g.). This crystallised from alcohol in prisms, m. p. 258° (Found: N, 4·1. $C_{18}H_{17}O_4N$ requires N, 4·5%). The benzene-soluble part gave homoanisic acid, m. p. 84°.

The nitrile [I; Ar = 3,4-$(MeO)_2C_6H_3$] was hydrolysed as above to α-(3,4-*dimethoxybenzylideneamino*)-3,4-*dimethoxycinnamic acid*, m. p. 260°. This was purified by dissolving it in sodium hydroxide and reprecipitating it with dilute hydrochloric acid as it was highly insoluble in all solvents (Found: N, 3·7. $C_{18}H_{19}NO_6$ requires N, 4·1%).

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[*Received, August 29th,* 1960.]

XUM

215. *Some New Di- and Tri-nitro-*p*-terphenyls.*

By G. W. Gray and D. Lewis.

Preparations and, where necessary, proofs of structure are described for five new dinitro- and three new trinitro-*p*-terphenyls—2,2′-, 2,3′-, 2,2″-, 2,4″-, and 4,2′-dinitro-*p*-terphenyl, and 2,2′,2″-, 2,2′,4″-, and 2,3′,4″-trinitro-*p*-terphenyl. Account being taken of the known 4,3′- and 4,4″-dinitro- and 4,2′,4″-trinitro-*p*-terphenyl, all the di- and tri-nitro-isomers likely to be formed in significant amount by direct nitration of the hydrocarbon in organic solvents have now been characterised.

Methods for preparing 2-, 2′-, and 4-nitro-, 4,4″-dinitro-, and 4,2′,4″-trinitro-*p*-terphenyl by nitration of the hydrocarbon have been discussed recently,[1] and it was decided to undertake quantitative work on the ratios of the nitro-isomers which are produced under various conditions for the mono-, di-, and tri-nitration of *p*-terphenyl. Apart from the work of France, Heilbron, and Hey [2] who proved the constitutions of 4,3′- and 4,4″-dinitro- and 4,2′,4″-trinitro-*p*-terphenyl, nothing was however known about other di- and tri-nitro-*p*-terphenyls which may be formed in significant amount by direct substitution of the hydrocarbon in organic solvents. Such products were required as reference compounds for the quantitative studies, and the syntheses and, where necessary, the proofs of structure of five new dinitro- and three new trinitro-*p*-terphenyls are now described. In selecting the particular compounds for study, it was assumed that the deactivating effect of a nitro-group would retard the entry of a second nitro-group into a ring until the other two rings in the *p*-terphenyl molecule had themselves been mononitrated. Compounds containing two or more nitro-groups in a given ring were not therefore studied. Moreover, substitution in the 3- and the 3″-position was considered unlikely, since a biphenylyl or nitrobiphenylyl group is *ortho* : *para*-directing. The exclusion of 3- and 3″-nitro-derivatives has been vindicated by quantitative data [3] for the mononitration of *p*-terphenyl, no 3-nitro-*p*-terphenyl being detected in the products.

The eight new nitro-*p*-terphenyls, together with 4,3′- and 4,4″-dinitro-, and 4,2′,4″-trinitro-*p*-terphenyl, and the hitherto unknown 3,4″-dinitro-*p*-terphenyl (isolated from an isomeric mixture) are shown in the chart, which also summarises the preparative routes employed.

Condensation of 4-nitro-4′-*N*-nitrosoacetamidobiphenyl with nitrobenzene yielded the three possible isomers, of which (III) had already been characterised by France, Heilbron, and Hey.[2] The constitution of isomer (VI) was confirmed when no m. p. depression was obtained on admixture with the product obtained by condensing 2-nitro-4′-*N*-nitroso-acetamidobiphenyl and nitrobenzene and when the infrared spectra of the two compounds were found to be identical. The identity of the isomer (V) followed by elimination, but was also proved when the same compound was prepared by deaminating 4-amino-3,4″-dinitro-*p*-terphenyl.

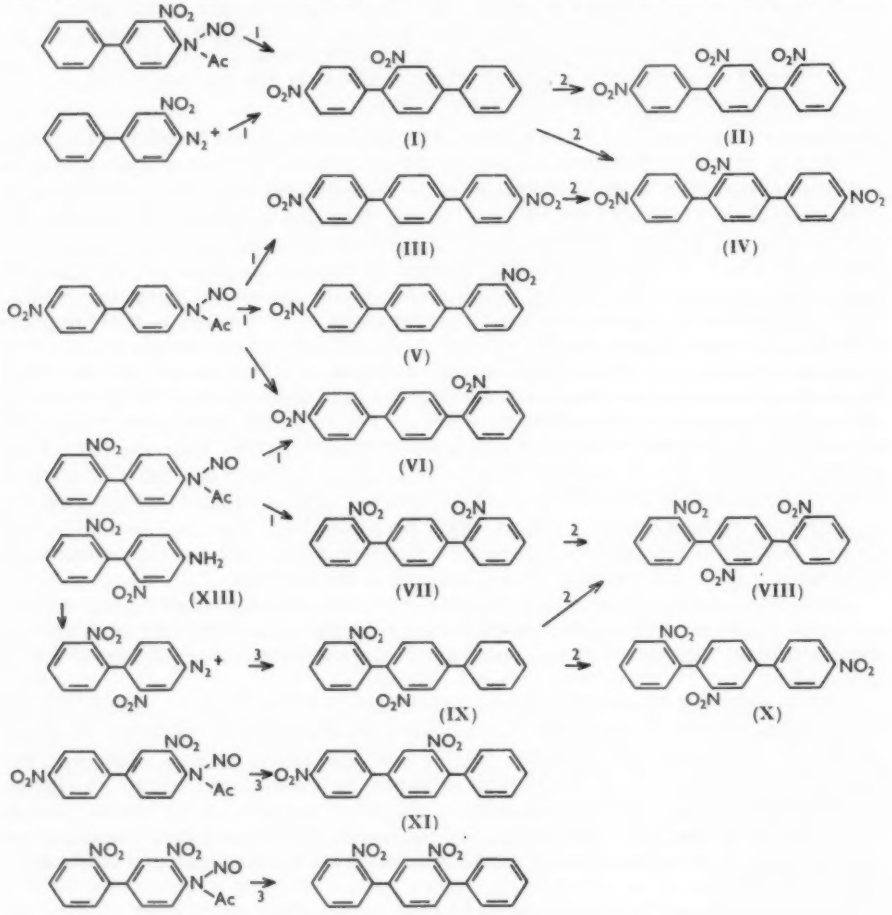
The dinitro-isomer (VII) was identified by its further nitration, in good yield, to the trinitro-isomer (VIII). The syntheses of isomers (XI) (a known compound [2]) and (XII) were unambiguous.

Preparation of the 2,2′-dinitro-isomer (IX) was particularly difficult, and attempts to obtain it by condensation of 3-nitro-4-*N*-nitrosoacetamidobiphenyl and nitrobenzene or by the Gomberg reaction between the corresponding amine and nitrobenzene failed. Yet, from both reactions, the isomeric 4,2′-dinitro-*p*-terphenyl (I) was obtained. The preparation of 4-amino-2,2′-dinitrobiphenyl (XIII) was then undertaken, to make possible the preparation of the dinitroterphenyl (IX) by the Gomberg reaction with benzene. Attempts to prepare this amine by selective reduction of 2,4,2′-trinitrobiphenyl and by

[1] Culling, Gray, and Lewis, *J.*, 1960, 1547.
[2] France, Heilbron, and Hey, *J.*, 1938, 1364.
[3] Gray and Lewis, unpublished work.

XUM

dinitration of 4-aminobiphenyl in concentrated sulphuric acid were unsuccessful. The latter failure is surprising, since 2-aminobiphenyl is readily nitrated under similar conditions.[4] The dinitro-amine (XIII) was finally obtained by nitrating 4-amino-2′-nitrobiphenyl in concentrated sulphuric acid, according to the method of Finzi and Bellavita,[5] who quoted no yields, but " estimated " the ratio of nitration at the 2- and 4′-position



Reagents: 1, $Ph{\cdot}NO_2$. 2, HNO_3. 3, C_6H_6.

as 40 : 60. We have actually isolated 41% of the amine (XIII), but could obtain no more than 25% of 4-amino-2′,4′-dinitrobiphenyl. It should be noted that since this work was carried out, Arcos, Arcos, and Miller [6] have isolated from this reaction 55% of the amine (XIII) and 25% of 4-amino-2′,4′-dinitrobiphenyl. From both pieces of work it is clear that more nitration occurs at the 2-position than was estimated by Finzi and Bellavita.[5] It is of interest that we could detect none of the expected, but as yet uncharacterised, 4-amino-2′,6′-dinitrobiphenyl in the product.

[4] Smith and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 2439.
[5] Finzi and Bellavita, *Gazzetta*, 1938, **68**, 77.
[6] Arcos, Arcos, and Miller, *J. Org. Chem.*, 1956, **21**, 651.

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Preparations of the unknown trinitro-isomers (II, VIII, and X) were not attempted by Gomberg reactions between the appropriate 4-aminodinitrobiphenyls and nitrobenzene, as it was foreseen that the separation of the isomeric mixtures would be difficult. Indeed, such syntheses are not necessary, for the mononitration of compound (VII) will give almost exclusively compound (VIII), which is therefore characterised by this reaction. Moreover, this compound (VIII) will also be formed, with its isomer (X), by the nitration of 2,2′-dinitro-*p*-terphenyl (IX). And the mononitration of 4,2′-dinitro-*p*-terphenyl (I) gives only the trinitroterphenyl (II) and the known compound (IV). The two binary mixtures of the trinitro-isomers were readily separated into their components, and isomers (VIII) and (IV) having been characterised, the identities of (II) and (X) followed by elimination. The two samples of compound (VIII), obtained by different routes, were shown to be identical by comparison of their infrared spectra, and by the absence of any m. p. depression on admixture of the two specimens.

Experimental

General Procedure for the Nitrosation of Acetylamines.—Acetylamines were nitrosated with nitrosyl chloride in acetic acid–acetic anhydride and condensed with benzene or nitrobenzene as described by Gray and Worrall [7] for the nitrosation of 3-fluoro- and 3-iodo-4-octyloxyacetanilide and the condensation with methyl benzoate.

4,2′-*Dinitro*-p-*terphenyl.*—4-Acetamido-3-nitrobiphenyl, m. p. 131—132°, was obtained in 76% yield by the method of Campbell, Anderson, and Gilmore [8] for the nitration of 4-acetamidobiphenyl. Their yield of 92% was not realised, partly because some dinitration occurred, as shown by the isolation of some 4-acetamido-3,4′-dinitrobiphenyl, m. p. 237—240°, from the liquors of the crystallisation of the 3-nitro-isomer.

(a) N-*Nitrosoacetylamine reaction.* 3-Nitro-4-*N*-nitrosoacetamidobiphenyl was obtained as a brown viscous oil by carrying out the general nitrosation procedure on the acetylamine (23 g.). Condensation with nitrobenzene (500 ml.) was allowed to proceed at room temperature for 4 days. The residue (24·5 g.), on removal of the nitrobenzene, was dissolved in benzene and adsorbed on a column (41 × 4·9 cm.) of alumina (750 g.). The first volume of eluate (350 ml.) yielded a red glass, and the next three fractions (total volume, 800 ml.) an orange-yellow solid (3·6 g.), m. p. up to 138°. Attempts to crystallise a product from the glass were unsuccessful, and further chromatography was employed to separate more of the orange-yellow solid (0·75 g.) from the gummy components. The combined fractions of the orange-yellow solid (4·35 g.) were dissolved in benzene (10 ml.), and light petroleum (b. p. 40—60°; 8 ml.) was added to the hot solution, which was then cooled. The thick supernatant liquid was decanted from the crystals which were crystallised from benzene and then from acetic acid. The yield of 4,2′-*dinitro*-p-*terphenyl*, m. p. 158—159°, was 6% (Found: C, 67·7; H, 3·8; N, 8·9. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%). The dinitro-isomer was characterised by further nitration, one of the two trinitro-isomers isolated being the known 4,2′,4″-trinitro-*p*-terphenyl.[1]

Solid products were also obtained from other fractions from the various chromatograms. These solids melted between 82° and 144° and analysed as dinitro-*p*-terphenyls, but no pure 2,2′- or 3,2′-dinitro-*p*-terphenyl could be isolated from these materials.

(b) *Gomberg reaction.* 4-Amino-3-nitrobiphenyl [8] was diazotised and condensed with nitrobenzene essentially as described for the preparation of 2′-nitro-*p*-terphenyl.[1] To minimise acetylation of the nitro-amine, the nitrosylsulphuric acid (90 ml.) was added all at once to the amine sulphate, prepared by mixing the amine (21·4 g.) and concentrated sulphuric acid (21·4 ml.) at room temperature. The acetic acid (107 ml.) was then added slowly to the cooled, stirred mixture, which was poured on ice 1 hr. after completion of the addition. The Gomberg reaction mixture was worked up after 40 hr., but the emulsified organic layer was difficult to separate and dry. The nitrobenzene was removed under reduced pressure (2 mm.), and part (19·7 g.) of the residue was digested with boiling benzene (100 ml.). The filtrate from the cooled extraction was adsorbed on alumina (130 g.), and the first fraction (50 ml.) to be eluted contained a red glass (2·11 g.). This material was dissolved in benzene (32 ml.) and readsorbed on alumina (47 g.), and from the first volume (110 ml.) of red eluate was again obtained a

[7] Gray and Worrall, *J.*, 1959, 1545.
[8] Campbell, Anderson, and Gilmore, *J.*, 1940, 449.

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glass (1·26 g.) which could now be crystallised, first from benzene–light petroleum (b. p. 40—60°) and then from benzene. The pale yellow spherulites of 4,2′-dinitro-*p*-terphenyl (1%), m. p. 158—159°, gave no m. p. depression on admixture with the same product obtained by method (a).

All other products from the first chromatogram decomposed on heating, and although an extremely small amount of a red crystalline compound, m. p. 234—236·5°, was obtained from the last fraction of the second chromatogram, no 2,2′- or 3,2′-dinitro-*p*-terphenyl was isolated from this preparation.

2,4″-, 3,4″-, *and* 4,4″-*Dinitro*-p-*terphenyls*.—4-Acetamido-4′-nitrobiphenyl [1] (14·6 g.) was nitrosated in the usual way [7] and condensed with nitrobenzene (700 ml.) by stirring for 19 hr. After removal of the nitrobenzene under reduced pressure, part (15 g.) of the residue was distilled at 0·06 mm. Two oily fractions which set to yellow solids, (8·2 g.) b. p. 250—260°, and (0·95 g.) b. p. 260—300°, were collected before the residue suddenly carbonised at a bath temperature of 330°. Part (5·9 g.) of the lower-boiling fraction, m. p. 151—177°, was dissolved in benzene and the solution concentrated to 100 ml. The suspension was cooled, and the yellow solid (1·86 g.), m. p. 209—228°, was thrice crystallised from acetic acid to yield 4,4″-dinitro-*p*-terphenyl (0·65 g.), m. p. 272—274·5°. This m. p. was undepressed on admixture of the product with the 4,4″-dinitro-isomer obtained by nitration of the hydrocarbon. The acetic acid liquors from the first crystallisation contained mainly 4-acetamido-4′-nitrobiphenyl (4—8%).

The benzene solution from the extraction of the low-boiling fraction was passed through a column (34 × 1·7 cm.) of alumina, and the broad, pale yellow region was eluted with benzene. The products obtained on evaporation of the first three fractions (50, 50, and 75 ml.; m. p. limits respectively 130—133°, 124—130°, and 109—128°) were dissolved separately in benzene and adsorbed on alumina (column dimensions, 63 × 1 cm.). The first of the above products was not improved, but the other two were separated from an impurity (A) (0·22 g.), and the m. p.s rose to 130—133°. The combined material (2·52 g.), m. p. 130—133°, was crystallised from ethanol and yielded large yellow blades of 2,4″-*dinitro*-p-*terphenyl* (2·29 g.), m. p. 132—133° (Found: C, 67·45; H, 4·1; N, 8·6. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%). Crystallisation from benzene raised the m. p. to 133°. This isomer was identified when the same product was isolated after condensation of 2-nitro-4′-*N*-nitrosoacetamidobiphenyl and nitrobenzene.

The material A was added to the product (0·09 g.), m. p. 117—187°, obtained from the fourth fraction (100 ml. of eluate) from the original chromatogram, and dissolved in benzene. Further chromatography on alumina gave various fractions of which the first and the last from the column (66 × 1 cm.) were respectively 2,4″-dinitro-*p*-terphenyl (0·08 g.) and 4,4″-dinitro-*p*-terphenyl (0·01 g.). The intermediate fractions yielded a product (0·1 g.), m. p. 147—157°, which was crystallised four times, alternately from benzene and ethanol. The m. p. of the 3,4″-*dinitro*-p-*terphenyl* remained constant at 160° from the last three of these crystallisations, although the melt was slightly turbid until 161°. This isomer (Found: C, 67·3; H, 4·2; N, 8·8%) was also obtained by deamination of 4-amino-3,4″-dinitro-*p*-terphenyl. The overall yields of the 2,4″-, 3,4″-, and 4,4″-dinitro-*p*-terphenyl were 17%, 0·4%, and 6% respectively.

3,4″-*Dinitro*-p-*terphenyl*.—Nitrosylsulphuric acid (5·7 ml., *ca.* 1·55 equiv.) [from a solution prepared in the usual way from powdered sodium nitrite (2·07 g.) and concentrated sulphuric acid (16·6 ml.)] was added during 18 min. to a stirred suspension of powdered 4-amino-3,4″-dinitro-*p*-terphenyl [9] (2·23 g.) in acetic acid (10 ml.). The temperature was maintained at 20° during the addition and for 30 min. after its completion. Diazotisation was only partly successful because of the low solubility of the amine sulphate, but 31% w/w aqueous hypophosphorous acid (12·7 ml., 10 equiv.) was then added, the temperature being kept about 20°. After the reaction mixture had been held at 4° for 36 hr., a positive coupling reaction was given, and it was necessary to heat the suspension for 24 hr. at 50° to complete deamination. The solid was filtered off, washed with water, 5N-ammonia, and again water, and dried. A portion (1 g.) of this purple-brown solid (2·02 g.) was refluxed with benzene (50 ml.), and, after cooling, the insoluble matter was filtered off. The filtrate was passed through a column (22 × 2·2 cm.) of alumina, and the chromatogram was developed with benzene. The broad yellow zone, lying under a red band (unchanged dinitro-amine), was eluted in 50—100 ml. fractions. The

[9] Culling, Gray, and Lewis, *J.*, 1960, 2699.

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solids (0·08 g.) from the first two volumes of eluate melted rather higher, 169—170° and 162—166°, than the products (total weight, 0·25 g.), m. p. limits 159—160·5°, obtained from fractions 3—10. Fraction 11 (400 ml. of eluate) gave material (0·02 g.) of m. p. 156—158°. Fractions 3—10 were combined and crystallised twice from benzene and twice from s-butyl alcohol, giving pale yellow crystals, m. p. 161—162° (Found: C, 67·3; H, 3·6; N, 9·0%). The total yield of 3,4″-dinitro-*p*-terphenyl, after one crystallisation, was 20%, and this product gave no depression of the m. p. on admixture with the same isomer, m. p. 160—161°, obtained by the *N*-nitrosoacetylamine reaction.

2,4″- *and* 2,2″-*Dinitro*-p-*terphenyl*.—2-Nitro-4′-*N*-nitrosoacetamidobiphenyl was prepared by the general nitrosation procedure from the acetylamine [1] (20 g.), and condensed in the usual way with nitrobenzene (500 ml.), the mixture being stirred for 2 days. The solvent-free residue (22·3 g.) was adsorbed from benzene (600 ml.) on a column of alumina (600 g.; 33 × 4·9 cm.). Development of the chromatogram with benzene gave three regions, which were, from the top of the column, brown (7 cm. thick), orange (5 cm.), and yellow (11 cm.). The material in the yellow band was eluted with benzene (3·5 l.) in fifteen fractions of approximately equal volume. Separation was poor, the m. p.s of the products ranging from 194—218° (first fraction) to 155—180° (last fraction). The fractions were combined (total wt., 10·4 g.) and crystallised four times from benzene. The mother-liquors were evaporated and the residue crystallised again. In this way a total yield of 2·5 g. (10%) of 2,2″-*dinitro*-p-*terphenyl*, m. p. 228—230·5°, was obtained (Found: C, 67·7; H, 3·6; N, 9·1. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%). The orientation of the nitro-groups was proved by further nitration to 2,2′,2″-trinitro-*p*-terphenyl, also obtained by nitration of 2,2′-dinitro-*p*-terphenyl.

The mother-liquors from the last crystallisation were adsorbed on alumina in an attempt to obtain the 2,3″- and the 2,4″-dinitro-isomer, but little separation was achieved (recovery from column, 96%). Adsorption on active carbon, with benzene, chloroform, or alcohol as solvents, gave a low recovery (20—35%), and only a little 2,2″-dinitro-isomer was isolated pure. The remaining material (4 g.) was sublimed at 10^{-3}—10^{-4} mm. Material of m. p. 110—176° (bath-temperature up to 162°) was discarded, and the second fraction (1·3 g.), m. p. 110—166° (bath-temperature 170°) was resublimed at 10^{-4}—10^{-5} mm.:

Bath-temp.	up to 130°	140°	154°	160°
Wt. of sublimate (g.)	0·1	0·3	0·7	0·15
M. p.	up to 179°	128—171°	114—162°	112—120°

The last fraction was crystallised twice from ethanol, yielding 2,4″-dinitro-*p*-terphenyl (0·07 g., equiv. to a yield of 0·6%), m. p. 132—133°. A third crystallisation raised the m. p. to 133° and gave bright yellow blades of 2,4″-dinitro-*p*-terphenyl (Found: C, 67·4; H, 4·0; N, 8·7%). A mixture with the same product (m. p. 133°) prepared by the *N*-nitrosoacetylamine reaction gave no depression of the m. p., and the infrared spectra of the solids were identical ($C-NO_2$ absorption bands occurred at 1353 and 1515 $cm.^{-1}$).

2,2′-*Dinitro*-p-*terphenyl*.—Powdered 4-amino-2′-nitrobiphenyl [1] (10 g.) was dissolved in 96% w/v sulphuric acid (100 ml.), kept at 15—20° by cooling. The stirred solution was maintained at −4° to −6° during the addition of ethyl nitrate (4 ml., 1·04 equiv.) and for 10 min. after the addition. The reactants were poured on ice (400 g.), and, the temperature being kept below 50°, the suspension was basified with aqueous ammonia (250 ml.; *d* 0·88). An attempt was made to crystallise the red precipitate (12 g.; m. p. 110—113°) according to the brief description given by Finzi and Bellavita.[5] This rather unsatisfactory process gave only 3% of orange-yellow 4-amino-2,2′-dinitrobiphenyl, m. p. 141—141·5°, and 3% of the red 4-amino-2′,4′-dinitrobiphenyl, m. p. 137·5—138·5°. A better procedure for the isolation of the 2,2′-dinitro-isomer is to crystallise the crude nitration product from a large volume (1·8 l.) of carbon tetrachloride, carrying out a hot filtration; a 41% yield is obtained on cooling to 31°. The material contained in the mother-liquors (the 2,2′- and 2′,4′-dinitro-isomers) was dissolved in benzene and chromatographed (alumina). In this way a 25% yield of the 2′,4′-dinitro-isomer was obtained. Finzi and Bellavita [5] record both isomers as melting at 138—139°.

Normal methods of acetylation gave 4-*acetamido*-2,2′-*dinitrobiphenyl* (97%), m. p. 124—130°, which is difficult to crystallise. From chloroform–light petroleum (b. p. 60—80°) (5 : 2) are obtained almost colourless crystals (60%), m. p. 134—135° (Found: C, 55·5; H, 3·7; N, 14·1. $C_{14}H_{11}N_3O_5$ requires C, 55·8; H, 3·7; N, 13·95%). The derivative is extremely light-sensitive.

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4-Amino-2,2′-dinitrobiphenyl (10·36 g.), 32% w/w hydrochloric acid (26 ml., 6·6 equiv.), and water (40 ml.) were warmed, and the suspension of the hydrochloride was cooled rapidly and diazotised at 0° to −5° with aqueous sodium nitrite (3·26 mol.) (addition time 2·5 hr.). Excess of nitrous acid was destroyed by sulphamic acid, benzene (500 ml.) was added, and the mixture was stirred and carefully basified with 40% aqueous sodium hydroxide (25 ml.) at 5—10°. Stirring was continued at room temperature for 48 hr., then the organic layer was separated, tar adhering to the walls of the flask being rejected. The washed and dried extract was concentrated to 45 ml. and passed over alumina (200 g.; 23 × 3·4 cm.). The nitro-compound (pale yellow band) was eluted in seven fractions with benzene (1·25 l.). The last fraction contained material (0·06 g.) of m. p. 80—104° and this was rejected. The remaining fractions were combined (4·43 g.; m. p. 100—109°) and crystallised from ethanol. The quality of the almost colourless 2,2′-*dinitro*-p-*terphenyl* (4 g., 31%), m. p. 109—110° (Found: C, 67·4; H, 3·5; N, 9·2. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%) was not improved by further crystallisation.

4,3′-*Dinitro*-p-*terphenyl*.—4-Acetamidobiphenyl (10·5 g.) was dinitrated [10] and the product crystallised from acetic acid (300 ml.) to give 4-acetamido-3,4′-dinitrobiphenyl (8·5—9·0 g.; m. p. 238—240°). 3,4′-Dinitro-4-*N*-nitrosoacetamidobiphenyl, prepared by the usual procedure from the acetylamine (10 g.), was filtered off after the nitrosation mixture had been poured into iced water. The nitroso-compound was pressed dry, and condensed in the usual manner with benzene (500 ml.) by stirring them for 5·5 days. A solution of the solvent-free residue in benzene was passed down a column of alumina (300 g.). The nitro-compound, eluted with benzene (2 l.), crystallised from benzene and then from acetic acid to yield slightly yellow 4,3′-dinitro-*p*-terphenyl (Found: C, 67·25; H, 4·0; N, 8·9%) (6%), m. p. 177—177·5°. France, Heilbron, and Hey [2] record the m. p. 174—175°.

2,3′-*Dinitro*-p-*terphenyl*.—The acetic acid liquors from the crystallisation of 4-acetamido-3,4′-dinitrobiphenyl were poured into water (1 l.), and the precipitate filtered off. Attempts to isolate pure 4-acetamido-3,2′-dinitrobiphenyl from this material, by crystallisation, were unsuccessful. The filtrate from a hot suspension of 15·5 g. of the product in benzene (260 ml.) was passed through a column of alumina (350 g.). Almost pure dinitroacetylamine (3—4 g.) was contained in the first 1·2 l. of eluate (benzene). Further elution (1 l.) gave impure material (1—2 g.) which was added to the chromatogram on the next batch of material. Crystallisation of the nearly pure material from alcohol and pyridine (3 : 1) gave bright yellow needles, m. p. 162—162·5°, in an overall yield of 11% (Found: C, 56·2; H, 3·5; N, 14·4. Calc. for $C_{14}H_{11}N_3O_5$: C, 55·8; H, 3·7; N, 13·95%). Finzi and Bellavita [5] record the m. p. 160—161°. 4-Acetamido-3,2′-dinitrobiphenyl was also obtained by nitrating 4-acetamido-2′-nitrobiphenyl according to the method [10] for the dinitration of 4-acetamidobiphenyl. The crude nitration product (94%) melted at 158·5—159°.

The acetyl derivative was readily hydrolysed by refluxing it for 15 min. with 70% w/w sulphuric acid, though Finzi and Bellavita [5] reported no deacetylation under such conditions. Alkaline hydrolysis of the acetylamine is, however, preferable: the acetylamine (0·54 g.) in ethanol (19 ml.) was treated according to the method [5] for hydrolysing 4-acetamido-3-nitrobiphenyl; the yield of 4-*amino*-3,2′-*dinitrobiphenyl* (orange-yellow needles), m. p. 170—170·5°, was 0·41 g. (88%), (Found: C, 55·8; H, 3·6; N, 16·0. $C_{12}H_9N_3O_4$ requires C, 55·6; H, 3·5; N, 16·2%).

2,3′-Dinitro-4′-*N*-nitrosoacetamidobiphenyl, prepared by the general nitrosation procedure from the acetylamine (15 g.), and isolated as described for 3,4′-dinitro-4-*N*-nitrosoacetamidobiphenyl, was condensed with benzene (500 ml.) by stirring them for 4 days. The solvent-free residue, dissolved in benzene, was adsorbed on a column of alumina (250 g.). The eluted nitro-compound was contaminated with an orange impurity, which was readily removed by further chromatography on alumina. The product crystallised from alcohol, yielding slightly yellow 2,3′-*dinitro*-p-*terphenyl* (6%), m. p. 118—119°. Further crystallisation raised the m. p. to 119·5—120·5° (Found: C, 67·2; H, 3·9; N, 8·8. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%).

Nitration of Dinitro- to Trinitro-p-*terphenyls*.—Fuming nitric acid (13 ml.; *d* 1·51) was added during 1—1·5 min. to a solution or suspension of the dinitro-compound (0·5 g.) in acetic acid (21·5 ml.), initially at 111° (bath-temperature 114°). The mixture was shaken occasionally and, after a total reaction time of 15 min., the solution was poured into water (70 ml.). After

[10] Le Fèvre and Turner, *J.*, 1928, 253.

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cooling, the precipitate (pale yellow or colourless) was filtered off, washed with water, 5N-aqueous ammonia, and again with water. The average yield of crude product was 98%.

4,2′,4″-Trinitro-p-*terphenyl.* The crude product, m. p. 189—191°, from the nitration of 4,4″-dinitro-*p*-terphenyl was crystallised from xylene (10 ml.), and washed with benzene. The yield of 4,2′,4″-trinitro-*p*-terphenyl,[1] m. p. 194—195°, was 0·46 g. (81%).

2,3′,4″- and 4,2′,4″-Trinitro-p-*terphenyl.* The crude product, m. p. 154°, from the nitration of 4,2′-dinitro-*p*-terphenyl (1 g.) was crystallised twice from benzene, yielding 4,2′,4″-trinitro-*p*-terphenyl (41%), m. p. 193·5—194° undepressed on admixture with the product obtained from 4,4″-dinitro-*p*-terphenyl. The infrared spectra of the two solids were identical ($C-NO_2$ absorption bands occurred at 1347 and 1520 $cm.^{-1}$).

The mother-liquors and the benzene washings from the first crystallisation were adsorbed on alumina (60 g., 26 × 1·7 cm.), and the chromatogram developed with benzene. The pale yellow colour of the adsorbed nitro-compounds was only just visible. The 2,3′,4″-trinitro-isomer was eluted first, and the best material, m. p. 178—180°, was contained in the fifth to tenth of the 50-ml. volumes of eluate collected. Crystallisation from benzene gave 2,3′,4″-*trinitro*-p-*terphenyl*, m. p. 179·5—180° (Found: C, 59·3; H, 2·9; N, 11·3. $C_{18}H_{11}N_3O_6$ requires C, 59·2; H, 3·0; N, 11·5%), in 23% yield.

2,2′,2″-Trinitro-p-*terphenyl.* The crude product, m. p. 158—159°, from the nitration of 2,2″-dinitro-*p*-terphenyl crystallised from benzene–light petroleum (b. p. 60—80°), to give the pale yellow, poorly crystalline 2,2′,2″-*trinitro*-p-*terphenyl*, m. p. 159—159·5° (Found: C, 59·3; H, 3·1; N, 11·7%), in 61% yield. This isomer is light sensitive.

2,2′,2″- and 2,2′,4″-Trinitro-p-*terphenyl.* Nitration of 2,2′-dinitro-*p*-terphenyl (1 g.) gave a low-melting product which crystallised from benzene. These crystals melted sharply at 148°, but the melt effervesced and this behaviour persisted after two further crystallisations from benzene. When this material was kept for one month, the m. p. gradually rose to 151—153°, and if it was melted on a microscope slide for a short time, the m. p. of the solidified melt was 164·5°, and the melt was clear. The occlusion of benzene in the crystals appeared to explain the melting behaviour, and the analytical figures (Found: C, 61·6; H, 3·3; N, 10·8. Calc. for $C_{18}H_{11}N_3O_6$: C, 59·2; H, 3·0; N, 11·5%) correspond to an approximate molar ratio of trinitro-compound to benzene of 3 : 1. When this material was crystallised from alcohol–acetone, or was dissolved in benzene or alcohol and recovered by rapid evaporation, the product melted from 150°. The upper m. p. was indefinite (>180°) owing to the dark colour and mistiness of the melt.

The crude product from a second nitration was crystallised four times from acetic acid. The m. p.s from the last three crystallisations were constant at 164°, but the melts were cloudy. Solvent occlusion may again be responsible for this behaviour, although the liquors from the second and third crystallisations slowly deposited pale yellow needles, m. p. 164—165°, giving a clear melt. The m. p. of 2,2′,4″-*trinitro*-p-*terphenyl* appears to be 164—165°, and a mixture of this product with 2,2′,2″-trinitro-*p*-terphenyl, m. p. 160—161°, also present in the crude nitration product, gave a large m. p. depression. The 2,2′,4″-trinitro-isomer (Found: C, 59·2; H, 3·4; N, 11·6. $C_{18}H_{11}N_3O_6$ requires C, 59·2; H, 3·0; N, 11·5%) is also very light-sensitive, and no accurate assessment of the yield can be given, because of the preparative difficulties encountered.

The liquors from the first crystallisation of the product from the first nitration were adsorbed on alumina (60 g., 26 × 1·7 cm.); elution was carried out with benzene, and 50 ml. fractions were collected. In view of the light-sensitivity of the material, it is imperative that the column should be covered with thick paper throughout the separation. The 2,2′,2″-trinitro-isomer was eluted first, and these fractions containing material of m. p. 158—159·5° were combined and evaporated to dryness, and the residue was crystallised from benzene. The 2,2′,2″-trinitro-*p*-terphenyl, m. p. 160—161° (Found: C, 59·3; H, 3·0; N, 11·5%), was obtained in 17% yield and was identical with the product, m. p. 159—159·5°, obtained by nitration of 2,2″-dinitro-*p*-terphenyl, as shown by a mixed m. p. and a comparison of the infrared spectra ($C-NO_2$ absorption at 1347 and 1515 $cm.^{-1}$).

The authors thank the Distillers Co. Ltd. and Imperial Chemical Industries Limited for grants to the Department, and one of them (D. L.) thanks the Hull Local Education Authority for a Maintenance Allowance.

THE UNIVERSITY, HULL. [*Received, September 6th*, 1960.]

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216. *Di-N-substituted 2-Halogenoethylamines. Part IV.*[1] NN-*Bis-2′-aryloxyethyl Derivatives: Syntheses, Reactivity, and Pharmacology.*

By J. F. Allen and N. B. Chapman.

The synthesis of compounds $(Ar{\cdot}O{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CH_2X,HX$ with X = Cl, Br, or I, and Ar = Ph, *o*-tolyl, or *p*-tolyl, is described. The mode of decomposition in acetone–water (2 : 1) at 30° of these compounds is reported and their pharmacological properties are briefly discussed. Evidence is provided that piperazinium salts formed by dimerisation of the halogenoamines are inactive against adrenaline and noradrenaline.

The present investigation concerned the influence of structure on reactivity, especially as to ethyleniminium ion formation, and on pharmacological properties in a series of adrenaline antagonists. We prepared the salts $(ArO{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CH_2X,HX$ where Ar = phenyl or *o*- or *p*-tolyl and X = halogen (except F). A *p*-methyl group decreases the pharmacological activity, but in the *ortho*-position enhances it (Gump and Nikawitz,[2] Graham [3]). Some of the intermediates, obtained by Gump and Nikawitz as oils, have now been obtained crystalline and characterised. Interaction of the appropriate 2-aryloxyethyl chloride or bromide with an excess of ethanolamine gave an *N*-monosubstituted derivative, which on further treatment with the same chloro-compound gave the required di-*N*-substituted hydroxy-amine, from which the corresponding halogeno-compounds were obtained by the method of Chapman and James.[4]

Experimental

Preparation of Materials.—*2-[Di-(2-aryloxyethyl)amino]ethanols.* Heating 2-chloroethyl-phenyl ether (1 mole) with 2-aminoethanol (6 moles) at the b. p. for 6 hr., followed by acidification, removal of unchanged 2-chloroethyl phenyl ether with ether, basification, and removal of dissolved ether with a current of air gave a wax. Pure 2-2′-phenoxyethylaminoethanol, m. p. 33·5—35° (cf. Gump and Nikawitz,[2] who obtained an oil), was obtained as white needles (83%) by adding 10% aqueous sodium hydroxide to a saturated aqueous solution of the crude product; this base gave a *picrate* (from ethanol), m. p. 114—115° (mixed m. p. with picric acid 92—112°) (Found: C, 47·2; H, 4·3; N, 14·1. $C_{16}H_{18}N_4O_9$ requires C, 46·8; H, 4·4; N, 13·7%), and a *hydrochloride* (from chloroform), m. p. 135—136° (Found: Cl, 16·2. $C_{16}H_{15}NO_2,HCl$ requires Cl, 16·3%).

Similarly were prepared the N-2′-o-*tolyloxyethyl analogue* (87%) [from light petroleum (b. p. 40—60°)], m. p. 62·5—63·5° (cf. ref. 2) (Found: C, 68·2; H, 8·9; N, 7·0. $C_{11}H_{17}NO_2$ requires C, 67·7; H, 8·8; N, 7·2%) [*picrate* (from ethanol), m. p. 118—119° (mixed m. p. with picric acid 94—116°) (Found: C, 48·5; H, 4·7; N, 13·2. $C_{17}H_{20}N_4O_9$ requires C, 48·1; H, 4·8; N, 13·2%)], and the -tolyl compound (77%) [from chloroform–light petroleum (b. p. 40—60°)], m. p. 52—52·5° [*picrate* (from ethanol), m. p. 115·5—116·5° (Found: C, 48·1; H, 4·7; N, 12·9%); *hydrochloride* (from chloroform), m. p. 156—157° (Found: Cl, 15·4. $C_{11}H_{17}NO_2,HCl$ requires Cl, 15·3%)].

Heating 2-2′-phenoxyethylaminoethanol (0·19 mole) suspended in 1 : 19 ethanol–water (100 ml.) with 2-chloroethyl phenyl ether (0·095 mole) at the b. p. for 80 hr., followed by working up as for the monophenoxyethyl compound, gave an oily mixture of mono- and bis-2′-phenoxyethyl compounds. The crystalline sulphate of the bis-compound separated after the oil had dissolved in dilute sulphuric acid. Liberation of the base followed by crystallisation from light petroleum (b. p. 40—60°) gave needles of 2-[di-(2-phenoxyethyl)amino]ethanol (85%), m. p. 35·5—36° (Found: C, 72·0; H, 7·8; N, 4·5. Calc. for $C_{18}H_{23}NO_3$: C, 71·8; H, 7·7; N, 4·7%). Gump and Nikawitz [2] reported this compound as an oil.

[1] Part III, Chapman and Allen, *J.*, 1960, 1482.
[2] Gump and Nikawitz, *J. Amer. Chem. Soc.*, 1950, **72**, 3846.
[3] Graham, *Brit. J. Pharmacol.*, in the press.
[4] Chapman and James, *J.*, 1953, 1865.

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2-[Di-(2-*o*-tolyloxyethyl)- (as an oil and as sulphate, 92%) and 2-[di-(2-*p*-tolyloxyethyl)-amino]ethanol [*hydrochloride* (85%) (from chloroform or dilute hydrochloric acid), m. p. 84·5—85° (Found: Cl, 8·95. $C_{20}H_{27}NO_3$,HCl,2H_2O requires Cl, 8·9%)] were similarly prepared by using the corresponding tolyloxyethyl bromides.

Halogeno-compounds. The following were prepared as described in Part I,[4] and except where otherwise stated were recrystallised from dry ethanol:

2-[Di-(2-phenoxyethyl)amino]ethyl chloride hydrochloride (from ethanol–ether; 97%), m. p. 128—129° (lit.,[2] 131°) (Found: Cl, 19·9. Calc. for $C_{18}H_{22}ClNO_2$,HCl: Cl, 19·9%); the *o*-tolyl analogue (from ethanol–ether; 60%), m. p. 141—142·5° (Found: Cl, 18·4. Calc. for $C_{20}H_{26}ClNO_2$,HCl: Cl, 18·6%); and the *p*-tolyl analogue (from ethyl acetate; 58%), m. p. 154—155° (lit.,[2] 148—151°) (Found: C, 52·4; H, 6·9; N, 3·7; Cl, 18·6. Calc. for $C_{20}H_{26}ClNO_2$,HCl: C, 52·5; H, 6·9; N, 3·6; Cl, 18·6%).

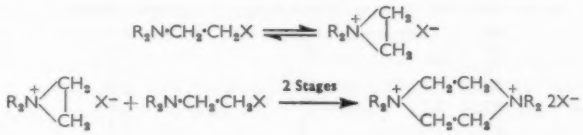
The corresponding *bromide hydrobromides*: *phenoxy* (89%), m. p. 115·5—116·5° (Found: C, 48·8; H, 5·6; H, 3·4; Br, 36·3. $C_{18}H_{22}BrNO_2$,HBr requires C, 48·6; H, 5·2; N, 3·2; Br, 35·9%); o-*tolyloxy* (62%), m. p. 164·5—165·5° (Found: C, 50·9; H, 5·4; N, 3·2; Br, 33·6. $C_{20}H_{26}BrNO_2$,HBr requires C, 50·7; H, 5·7; N, 3·0; Br, 33·8%); and p-*tolyloxy* (79%), m. p. 153·5—154·5° (Found: C, 51·1; H, 5·8; N, 3·0; Br, 33·8%).

The corresponding *iodide hydriodides*: *phenoxy* (70%), m. p. 152—152·5° (Found: C, 40·3; H, 4·5; N, 2·8; I, 47·2. $C_{18}H_{22}INO_2$,HI requires C, 40·1; H, 4·3; N, 2·6; I, 47·1%); o-*tolyloxy* (42%), m. p. 191—192: (Found: C, 42·6; H, 5·1; N, 2·7; I, 44·6. $C_{20}H_{26}INO_2$,HI requires C, 42·4; H, 4·8; N, 2·5; I, 44·7%); and p-*tolyloxy* (80%), m. p. 119·5—120·5° (Found: C, 42·5; H, 4·9; N, 2·2; I, 44·5%).

Procedure.—This was as described in Part II.[5] In reactivity experiments with the di-*p*-tolyloxy-chloride hydrochloride, diphenoxy-iodide hydriodide, and di-*p*-tolyloxy-iodide hydriodide, crystalline salts were precipitated and were isolated. These are very probably *piperazinium salts* formed by dimerisation of the halogenoamines in the usual way but they were not fully characterised. The three products had respectively m. p. 230—231° (Found: Cl, 10·5. $C_{40}H_{52}Cl_2N_2O_4$ requires Cl, 10·2%), m. p. 240—241° (Found: C, 52·1; H, 5·34. $C_{36}H_{44}I_2N_2O_4$ requires C, 52·6; H, 5·4), and m. p. 244° (decomp.) (Found: C, 55·0; H, 6·0; N, 3·3; I, 29·0. $C_{40}H_{52}I_2N_2O_4$ requires C, 54·7; H, 5·9; N, 3·2; I, 28·9%).

Discussion

Fig. 1 shows curves typical of the decomposition of the chloro-compounds of this group, and Fig. 2 curves typical of the decomposition of the bromo- and iodo-compounds. These curves show the usual general pattern. It seems likely that with some of the compounds of this group piperazinium salt formation according to the following scheme plays a significant rôle in the decomposition (cf. above):



The ethyleneiminium ion is also hydrolysed, as can be seen from the development of titratable acidity in the system. However, the concentration of halide produced at any given time will now, if no other reactions occur, be equal to the sum of the free ethyleneiminium-ion concentration, the hydrogen-ion concentration, and twice the piperazinium salt concentration. The curves in Figs. 1 and 2 allow us, therefore, to set an upper limit to the concentration of piperazinium salt at any given time.

Although it has not been possible so far to synthesise these piperazinium salts directly, and so to study their pharmacological properties, pharmacological testing[3] of suitable

[5] Chapman and James, *J.*, 1954, 2103.

aged solutions of the halogenoethylamines, which almost certainly contain these piperazinium salts, has shown that, in agreement with previous observations, the piperazinium salts have no detectable anti-adrenaline activity.

Application of Belleau's [6] theory to *N*-alkyl-*N*-aryloxyethyl-2-halogenoethylamines leads to the conclusion that *o*- and possibly *p*-methyl groups in the aryloxy-residue should enhance activity. Similar conclusions for bisaryloxyethyl compounds seem reasonable. The results assembled in the Table confirm such conclusions for these compounds, save for the *p*-tolyloxy-derivative among the chloro-compounds, and the *o*-tolyloxy-derivative

FIG. 1. FIG. 2.

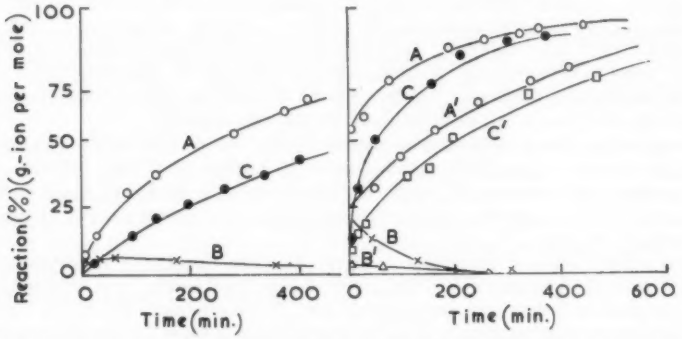


FIG. 1. *Decomposition of* 2-[*di*-(2-*phenoxyethyl*)*amino*]*ethyl chloride at* 30° *in aqueous acetone.* (A) *Chloride ion liberated.* (B) *Ethyleneiminium ion formed.* (C) *Hydrogen ion formed.*

FIG. 2. *Decomposition of* 2-[*di*-(2-o-*tolyloxy*)*amino*]*ethyl bromide and iodide at* 30° *in aqueous acetone.* A, B, C, *refer to the bromide, and* A′, B′, C′ *to the iodide; otherwise as for* Fig. 1

among the iodo-compounds, but clearly the observations are marginal and may well be complicated, as has previously been shown,[1] by differing efficiencies of utilisation of ethyleneiminium ions *in vivo*. Finally we note that there is only a rough qualitative correlation between maximum concentration of ethyleniminium ion *in vitro* and anti-adrenaline and -noradrenaline activity *in vivo* (see Table).

Reactions and properties of salts $(Ar{\cdot}O{\cdot}CH_2{\cdot}CH_2)_2{\cdot}N{\cdot}CH_2{\cdot}CH_2X,HX$.

Compound Ar	X	Proportion of X liberated * (%) after ~360 min.	Max. proportion of ethyleniminium ion formed * (%)	Anti-adrenaline activity † (micromoles/kg.)	Anti-noradrenaline activity † (micromoles/kg.)
Ph	Cl	59	6	4·6	7·6
Ph	Br	93	33	2·2	4·5
Ph	I	70	7	3·0	5·6
o-Tolyl	Cl	48	4	3·0	3·6
,,	Br	91	21	1·0	1·5
,,	I	74	3	3·9	6·8
p-Tolyl	Cl	56	6	7·3	12·4
,,	Br	93	27	1·7	2·8
,,	I	—	—	1·2	2·0

* G.-ion/mole. † $E.D._{50}$ in spinal rats.

We thank the Department of Scientific and Industrial Research for a maintenance grant (J. F. A.) and Imperial Chemical Industries Limited for a grant for microanalyses and materials. The collaboration of Dr. J. D. P. Graham and colleagues is gratefully acknowledged.

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[*Received, September* 19*th*, 1960.]

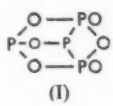
[6] Belleau, *Canad. J. Biochem. Physiol.*, 1958, **36**, 731.

217. *The Preparation and Methods of Determination of Hypophosphate.*

By W. G. Palmer.

Details are given of an expeditious method of preparing sodium hypophosphate decahydrate from red phosphorus and bleaching powder. Several novel methods for the analytical determination of hypophosphate are described and exemplified: the restriction of its oxidation by aqueous bromine to a narrow range of pH is explained. Evidence is given that the crude product of the oxidation contains the calcium salt of a previously unrecognized dibasic acid of probable formula $H_2P_4O_7$.

All known means of obtaining hypophosphates depend on the wet oxidation of elementary phosphorus. Hypochlorites and chlorites[1] afford comparable yields, but with these reagents, as with others, at least 50% of the total phosphorus is converted into orthophosphate. Use of the readily accessible hypochlorite, bleaching powder, to gain maximum yield has not been reported, but a satisfactory procedure is now described. In view of the macromolecular constitution of red phosphorus it seems improbable that the products of its controlled oxidation would be limited to those containing in their molecules two atoms at most of phosphorus. Analysis of the calcium salts obtained as the immediate result of oxidation revealed the probable existence of at least one previously unknown acid, of apparent formula $H_2P_4O_7$, but no means of separation or of increasing its proportion were found. The anhydride of this acid is presumably an isomer of phosphorous anhydride, and might tentatively be assigned the structure (I).



(I)

During the preparation of a series of hypophosphates the hitherto unrecorded ceric salt, CeP_2O_6, was obtained as a yellow hydrated gel; it is probably even more resistant to attack by acids than is thorium hypophosphate.[2]

Determination of Hypophosphate.—There has been a serious lack of reliable methods, adaptable to differing conditions, for the determination of hypophosphate in the presence of other phosphorus oxy-anions. The following have now been tested and proved serviceable: (1) Oxidation by iodic acid at 100° in the presence of 40% sulphuric acid (hypophosphate is stable to iodic acid under the conditions of Andrews's method of titration). (2) Precipitation as $Ag_4P_2O_6$ from a medium that may contain up to 0·5M-nitric acid. (3) Precipitation as $Zn_2P_2O_6$ at pH 4, followed by conversion of this precipitate into $Ag_4P_2O_6$. (4) Oxidation by aqueous bromine in the pH range 6—9 (maximum rate of oxidation at pH 7·7).

Methods (1) and (2) are simple and expeditious but not available in the presence of other reducing oxy-anions of phosphorus. Such oxy-anions may, however, readily be separated by methods (3) and (4). Method (2), in 0·5M-nitric acid, separates hypophosphate completely from ortho-, di-, and tri-phosphate, and from trimetaphosphate: tetra- and poly-metaphosphate interfere. Since hypophosphite and phosphite are oxidized by molecular bromine in freely acid solution,[3] whereas hypophosphoric acid is oxidized only in the range pH 6—9, method (4) offers a means of distinguishing the latter acid.

The interaction of hypophosphate with bromine in aqueous solution merits attention for further reasons. Salzer noticed that, although aqueous bromine had no action upon hypophosphoric acid, yet it readily oxidized the tetrasodium salt.[4] Blaser and Halpern correlated rate of oxidation at 20° with the pH of the solution.[5] Their results, presented as percentage of hypophosphate oxidized in a fixed time by 0·1N-aqueous bromine, are plotted

[1] Leininger and Cholski, *J. Amer. Chem. Soc.*, 1949, **71**, 2385; *Inorg. Synth.*, 1953, **4**, 68.
[2] Moeller and Quinty, *J. Amer. Chem. Soc.*, 1952, **74**, 6123.
[3] Griffith and McKeown, *Trans. Faraday Soc.*, 1933, **29**, 611; 1934, **30**, 530.
[4] Salzer, *Annalen*, 1886, **232**, 114.
[5] Blaser and Halpern, *Z. anorg. Chem.*, 1933, **215**, 33.

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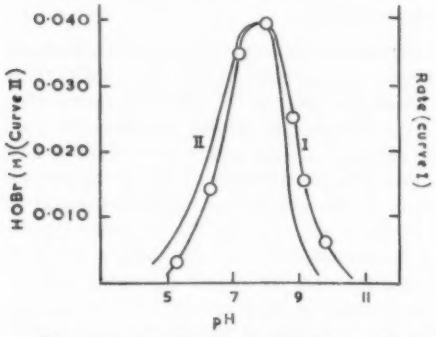
in curve I in the Figure. With the assumptions that at 20° the hydrolysis constant of bromine [6] is $4{\cdot}2 \times 10^{-9}$, the acid dissociation constant of hypobromous acid [7] is $2{\cdot}1 \times 10^{-9}$, and that the concentration of tribromide ion is negligible, the concentration of hypobromous acid in the range of pH studied by Blaser and Halpern has been calculated and plotted as curve II. The identity of the sharp maxima at pH 7·7 and the coincidence in form of the curves leave little doubt that hypobromous acid is the effective oxidant. The product of concentrations [HOBr][BrO^-], which would be significant for oxidation by bromous acid, has a maximum at pH 8·5 and values appreciably different from zero only in the narrow pH range 7—9. The oxidation of hypophosphate by bromine is thus analogous to the interaction of oxalate with bromine.[8]



Curve I: *rate of oxidation of* $P_2O_6^{4-}$, *on an arbitrary scale* (Blaser and Halpern).
Curve II: *concentration of* HOBr (mole/l.) *when total concentration of* Br_2 *is* 0·1N.

Blaser and Halpern were led to believe that the product of the oxidation is largely, if not exclusively, diphosphate. By a rather more stringent analytical procedure their results have been fully confirmed. $P_2O_6^{4-}$, oxidized by aqueous bromine in the presence of excess of sodium hydrogen carbonate, is converted to the extent of at least 97% into $P_2O_7^{4-}$. This observation need not necessarily imply that $P_2O_6^{4-}$ contains an oxygen bridge between the phosphorus atoms. The hypophosphate species is mainly $HP_2O_6^{3-}$ in the range of pH concerned,[9] and the first reaction is $HP_2O_6^{3-} + HOBr = 2PO_3^- + Br^- + H_2O$; but, the monomeric ion PO_3^- being unstable, this action is followed, before the ions escape from contiguity, by the hydration $2PO_3^- + H_2O = H_2P_2O_7^{2-}$. As it is now known that polythionate ions contain simple chains of sulphur atoms,[10] a similar situation must be assumed to arise when sulphur atoms are removed from these ions by cyanide or sulphite, with the quantitative formation of trithionate (see also following paper).

Experimental

Preparation of Tetrasodium Hypophosphate, $Na_4P_2O_6,10H_2O$.—By means of an adjustable siphon the filtered extract from 100 g. of bleaching powder by 425 ml. of water, cooled to 10°, is run into a stirred mixture of 10 g. of red phosphorus (free from phosphoric acid) with 100 ml. each of water and 3M-acetic acid, cooled in a bath of ice and water. During the oxidation (normally completed in 30 min.) the temperature of the mixture should be 15—25°. The oxidation is very rapid: if addition of hypochlorite is interrupted the liquid ceases to bleach litmus within a few seconds. Test experiments with pure hypophosphate show that it suffers no oxidation under the conditions described.

To the colourless, well-stirred filtrate from excess of phosphorus (5 g.), 20% aqueous sodium hydroxide is slowly added until a permanent turbidity results (24—25 ml.). Addition of 40 g. of hydrated sodium acetate produces a copious white precipitate, which is filtered off. By this means about 85% of the orthophosphate produced in the oxidation remains in the filtrate and all the hypophosphate is recovered in the precipitate as $Ca_2P_2O_6,2H_2O$. The moist cake of solid

[6] Liebhafsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1500.
[7] Kelley and Tartar, *J. Amer. Chem. Soc.*, 1956, **78**, 5752.
[8] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 107.
[9] Schwarzenbach and Zure, *Monatsh.*, 1950, **81**, 202.
[10] Foss, Furberg, and Zachariasen, *Acta Chem. Scand.*, 1954, **8**, 459, 473.

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is introduced in portions into a mixture of 60 ml. each of 4N-sulphuric acid and ethanol, and the whole shaken until in about 15 min. all compact white masses have given place to a uniform crystalline deposit of $CaSO_4,2H_2O$; this is filtered off, and washed with a mixture of 2N-sulphuric acid and ethanol (10 ml. of each), the washings being added to the main filtrate. In the latter 40 g. of hydrated sodium acetate are forthwith dissolved, to produce a crystalline deposit, consisting of $Na_2H_2P_2O_6,6H_2O$ and some hydrated sodium sulphate, all orthophosphate surviving from the earlier stage being retained in the solution as NaH_2PO_4.

In a solution of the solid in 80—90 ml. of hot water, filtered if necessary, and cooled to 40°, 10 g. of sodium hydroxide are dissolved. The salt $Na_4P_2O_6,10H_2O$ crystallizes almost quantitatively during some hours. (Rapid cooling may cause co-deposition of sodium sulphate.) The crystals are washed three times with ice-cold 10% aqueous sodium hydroxide and then thoroughly with ethanol (yield 11·5 g.) [Found: loss at 110°, 41·4; total P, 14·2; P_2O_6 (as $Ag_4P_2O_6$), 35·7; (by HIO_3 oxidation), 35·8; Na_2SO_4, 0·4; phosphate, nil. Calc. for $Na_4P_2O_6,10H_2O$: H_2O, 41·4; P, 14·4; P_2O_6, 36·5%]. From a " model " solution, incorporating pure hypophosphate and imitating that resulting from an actual oxidation, 90·0% of the hypophosphate was recovered as $Na_4P_2O_6,10H_2O$ by the procedure described.

Ceric Hypophosphate, CeP_2O_6,xH_2O.—On mixing equimolecular solutions in N-nitric acid of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, and sodium hypophosphate, *ceric hypophosphate* is obtained quantitatively as a yellow gel, which is separated and washed on the centrifuge (Found, in air-dried material: Ce, 37·4; P_2O_6, 42·7; H_2O, 19·9%; $P_2O_6/Ce = 1·010$. $CeP_2O_6,4H_2O$ requires Ce, 37·8; P_2O_6, 42·7; H_2O, 19·5%). The gel is unattacked by 1 hour's contact with 3N-nitric acid at 100°, but, like ceric phosphate, readily dissolves to a colourless solution on addition of hydrogen peroxide. At room temperature neither concentrated nitric nor sulphuric acid affects it, but if it is warmed with the latter acid and an equal volume of water is added a solution of ceric sulphate results. Although stable at 100° the gel begins to lose colour slowly at 130° and rapidly becomes colourless at 150° owing to the reaction $6CeP_2O_6 = Ce_4(P_2O_6)_3 + 2Ce(PO_3)_3$.

Determination of Hypophosphate.—(1) *Oxidation with iodic acid.* A sample of the hypophosphate (0·2—0·3 g.) is treated at 100° with a solution of potassium iodate (1 g.) in 40% sulphuric acid (25 ml.). Oxidation is usually complete in 1 hr., and the iodine produced is then distilled into aqueous potassium iodide and titrated. The theoretical equivalence ($I_2O_5 = 5P_2O_6^{4-}$, or 1 ml. of 0·02N-arsenite = 0·00790 g. of $P_2O_6^{4-}$) may be safely assumed.

(2) *Precipitation as* $Ag_4P_2O_6$. To a continuously stirred solution of hypophosphate (0·1—0·15 g.) in 0·5N-nitric acid (10 ml.), 10 ml. of a 10% solution of silver nitrate in 0·5N-nitric acid are added dropwise. After granulation by shaking, the precipitate, collected in a filter crucible, is washed once with a few ml. of the silver nitrate solution and then freely with ethanol. After a short drying at 100° the crucible is gradually heated until the originally cream-coloured content becomes uniformly grey in consequence of the reaction $Ag_4P_2O_6 = 2Ag + 2AgPO_3$, which occurs rapidly at 300° (Found: Ag, 73·4; P, 10·6. Calc. for $Ag_4P_2O_6$: Ag, 73·2; P, 10·5%).

A mixture of 0·1145 g. of KH_2PO_4 with 0·1227 g. of $Na_2H_2P_2O_6,6H_2O$ gave 0·2307 g. of final product (Calc. for the hypophosphate: 0·2306 g.). Similar tests with di-, tri-, trimeta-, tetrameta-, and polymeta-phosphate showed that only the last two interfere.

(3) *Precipitation as silver salt preceded by precipitation as zinc hypophosphate.* In this method the only common interfering phosphorus oxy-acid is diphosphate, which is also precipitated by the zinc reagent. The washed precipitate from 50 g. of pure zinc sulphate and 29 g. of sodium hydrogen carbonate is dissolved in hot aqueous acetic acid containing 31 ml. of glacial acid, and to the solution, diluted to 950 ml. with water, a further 115 ml. of glacial acetic acid are finally added. Of the solution so prepared 25 ml. are equivalent to 0·33 g. of $P_2O_6^{4-}$.

To a solution of hypophosphate (0·1—0·2 g.) in N-nitric acid (5—10 ml.) an equal volume of M-sodium acetate solution is added, followed at once by the zinc acetate reagent (50 ml.). After 30 min. the precipitate is separated in the centrifuge, washed twice with 20 ml. portions of the zinc reagent (not water), and then dissolved in the minimum of dilute nitric acid. From the solution, diluted to 100 ml., silver hypophosphate is precipitated by adding 1 g. of silver nitrate, and finally treated as in method (2). In a test conducted as described 0·1687 g. of $Na_2H_2P_2O_6,6H_2O$ gave 0·3130 g. of $Ag_4P_2O_6$ (Calc.: 0·3163 g.).

(4) *Oxidation by aqueous bromine (acting as* HOBr). Into a glass-stoppered bottle the following are introduced in succession: hypophosphate (0·2—0·25 g.) dissolved in N-hydrochloric acid

(20 ml.); potassium bromate solution (3 g. $KBrO_3$ per l.) (25 ml.); water (55 ml.) containing 5 drops of 2% solution of ammonium molybdate; and potassium bromide (1 g.). Immediately on the last addition the bottle is stoppered and its contents well mixed. A second bottle, similarly charged but without the hypophosphate, serves as control. After 30 min. each bottle is opened for a short time to receive 4·5 g. of pure borax (with precautions against loss of bromine), and when this has been dissolved the bottles are set aside for 1 hr.; finally, iodine released by addition of potassium iodide and sulphuric acid is titrated. A sample (0·2533 g.) of $Na_2H_2P_2O_6,6H_2O$ led to 16·05 ml. of 0·1N-thiosulphate as the difference in titrations of the two mixtures (Calc.: 16·13 ml.).

Product of oxidation of hypophosphate by hypobromous acid. Twice the theoretical amount, *viz.*, 30 ml. of 0·19N-bromine water, was added to a solution of $Na_2H_2P_2O_6,6H_2O$ (0·4110 g.) in water (25 ml.), followed by sufficient sodium hydrogen carbonate (3·5 g.) to saturate the system. After 2 hr. at room temperature the solution was made up to exactly 100 ml. and divided into two equal portions. Excess of bromine was removed by a current of air after addition of acetic acid (8·5 ml.) to each portion, and the precipitates then obtained by adding 30 ml. of zinc acetate reagent were collected and washed separately in the centrifuge. One precipitate was dissolved in 10 ml. of 3N-nitric acid, and the solution diluted to 100 ml. and heated on the water-bath for 1½ hr. From it orthophosphate was precipitated as phosphomolybdate and weighed as $Mg_2P_2O_7$. The zinc content of the second precipitate was then determined by conversion into $ZnNH_4PO_4$.

Calculation from the weights of $Mg_2P_2O_7$ and $ZnNH_4PO_4$ obtained (0·1379 g. and 0·2213 g., respectively) shows (i) that 95% of the phosphorus in the original hypophosphate is recovered in the $Mg_2P_2O_7$ derived from a zinc precipitate that can contain no orthophosphate; and (ii) that the Zn/P atomic ratio in the precipitates formed by zinc acetate reagent is 1·00. If the precipitates had contained $Zn_2P_2O_6$ derived from unchanged hypophosphate then this ratio would be greater than unity. Control experiments with pure diphosphate showed that 98% of $P_2O_7^{4-}$ is precipitated as $Zn_2P_2O_7$ from solutions at pH 4. When the results of the oxidation are corrected in the light of this information it appears that not less than 97% of hypophosphate is oxidized to diphosphate.

Composition of the Crude Calcium Salt Mixture resulting from Oxidation of Phosphorus.—The following summary of analytical operations upon this calcium salt mixture suggests that it contains a small proportion of the salt of a previously unknown acid $H_2P_4O_7$, which resembles hypophosphoric acid in that, under the conditions previously specified, the silver and the zinc salts are co-precipitated. The hypophosphate content of the mixture had therefore to be estimated from the known efficiency of the conversion into pure hypophosphate.

(1) Total calcium, 22·05%, estimated after converting all phosphorus compounds into orthophosphate by repeated evaporation to dryness with nitric acid.

(2) The precipitate produced by addition of zinc acetate reagent to a specimen of the mixture dissolved in N-nitric acid contained P, 16·8%, and the filtrate from the precipitate P, 3·04%, of the mixture taken. Total phosphorus, 19·84%. In the precipitate, containing as $Zn_2P_2O_6$ all hypophosphate originally present, the Zn/P ratio was 0·88.

(3) The silver salt precipitate, obtained as before described, contained P, 12·1%, and the ratio Ag/P was 1·70. Calculated total phosphorus as $Ca_2P_2O_6,2H_2O$ and $CaP_4O_7,2H_2O$ (see composition below) 0·0448 g.: recovered from the silver salt precipitate as $Mg_2P_2O_7$, 0·0445 g.

(4) The mixture contained no anions reducing mercuric chloride at room temperature, and therefore no phosphite, since the aqueous solubility of calcium hypophosphite excludes it from the mixture.

(5) Equivalent of the mixture in iodic acid oxidation: Found, 158 (Calc., assuming complete oxidation of $H_2P_4O_7$ to phosphoric acid: 152).

(6) From solutions at pH 0·125 and 0·6, 1 g. of the mixture reacted respectively with 5·9 ml. and 5·3 ml. of 0·1N-bromine during 1 hr.; at pH 3, during 2 hr., 4·6 ml. were taken up. The corresponding uptake by 0·575 g. of pure calcium hypophosphate (see composition below) was 0·2, 0·0, and 0·0 ml. respectively. These results suggest that the new acid is hydrolysed faster than hypophosphoric, to give compounds oxidized by molecular bromine, *e.g.*, phosphite.

The following approximate composition for the calcium salt mixture emerges: $Ca_2P_2O_6,2H_2O$, 57·5; $CaP_4O_7,2H_2O$, 9·4; $CaHPO_4,2H_2O$, 17·0; (gel) hydration lost at 100°, 15·3%.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January 19th*, 1960.]

218. β-*Aroylpropionic Acids. Part XIX.* Further Observation on the Fries Rearrangement.*

By A. M. El-Abbady, F. G. Baddar, and A. Labib.

Phenol and *p*-cresol, when heated with phenylsuccinic anhydride, give the corresponding aryl hydrogen phenylsuccinates, but *m*-cresol does not undergo this reaction.

When the two phenyl hydrogen phenylsuccinates are heated with aluminium chloride they give *p*-hydroxy-keto-acids, whereas the *p*-tolyl esters under similar conditions give *o*-hydroxy-keto-acids.

In continuation of our previous investigation,[1] the half-esters (I) obtained by the fusion of phenol and *p*-cresol with phenylsuccinic anhydride at 130—140° were subjected to the Fries rearrangement, so as to establish their structure and obtain more information about the mechanism of this reaction.

When phenol was fused with phenylsuccinic anhydride it gave a mixture of the isomeric phenyl hydrogen phenylsuccinate (Ia and b; Ar = Ph) in the ratio 2 : 3, respectively. The same mixture [poorer yield and higher percentage of acid (Ia)] was obtained when the reactants were treated with aluminium chloride in carbon disulphide.

When both half-esters (I; Ar = Ph) were heated with aluminium chloride in acetylene tetrachloride or in nitrobenzene at 117—120°, they gave β-*p*-hydroxybenzoyl-α- (VIa; X = C_6H_4) and β-phenylpropionic acid (VIb; X = C_6H_4), respectively. The structure of these acids (VI; X = C_6H_4) was established by converting them into the corresponding methoxy-acids (VIc and d; X = C_6H_4) which were identical with authentic specimens.[2] Replacement of acetylene tetrachloride by toluene gave rise to α- and β-phenyl-β-*p*-toluoylpropionic acids (VII) as the main product, together with traces of acids (VIa and b; X = C_6H_4).

p-Cresol and phenylsuccinic anhydride were similarly treated; they gave a mixture of the *p*-tolyl hydrogen esters (Ia and b; Ar = *p*-Me·C_6H_4) in 16 and 45% yield, respectively. When these half-esters were heated with aluminium chloride at 117—120° in acetylene tetrachloride or in nitrobenzene, they gave β-(2-hydroxy-5-methylbenzoyl)-α- (IIIa; R″O·X = 2,5-HO·C_6H_3Me) and -β-phenylpropionic acid (IIIb; R″O·X = 2,5-HO·C_6H_3Me), respectively. The structure of the former of these products (III) was established by converting it into its methyl ether methyl ester, which was identical with an authentic specimen prepared according to scheme B. 2′-Methoxy-5′-methylchalcone (VIIIa) with hydrogen cyanide gave the nitrile (IXa), which was hydrolysed with aqueous potassium hydroxide to the acid (IIIc; R″O·X = 2,5-MeO·C_6H_3Me), then methylated to the corresponding methyl ester. The structure of the isomer (IIIb; R″O·X = 2,5-HO·C_6H_3Me) was inferred from its analytical data and from the fact that its methyl ether methyl ester was different from the above authentic specimen.

When the *p*-tolyl half-esters (Ia and b) were heated with aluminium chloride in toluene, they gave a mixture of β-(2-hydroxy-5-methylbenzoyl)-α- and -β-phenylpropionic acid (IIIa and b; R″O·X = 2,5-HO·C_6H_3Me, respectively) and phenylsuccinic acid. No phenyl-β-*p*-toluoylpropionic acid was obtained. The isolation of phenylsuccinic acid indicates that part of the tolyl ester (Ia or b) remained unchanged at the end of the reaction.

Condensation of m-*Cresol and its Methyl Ether with Phenylsuccinic Anhydride.*—Attempts to prepare the *m*-tolyl hydrogen phenylsuccinates (Ia and b; Ar = *p*-Me·C_6H_4) by fusing

* Part XVIII, *J.*, 1961, 707.

[1] Awad, Baddar, and Marei, *J.*, 1954, 4538.
[2] Wali, Khalil, Bhatia, and Ahmed, *Proc. Indian Acad. Sci.*, 1941, **144**, 139.

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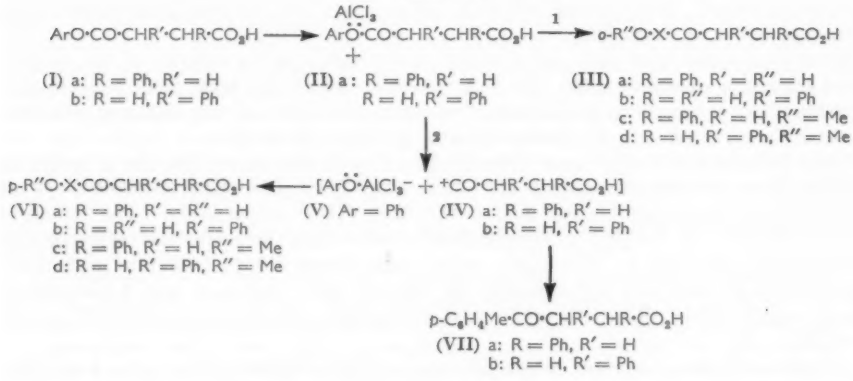
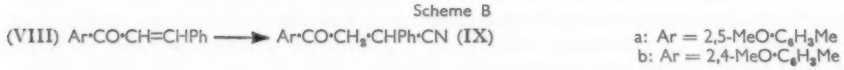
m-cresol with phenylsuccinic anhydride or treating their ice-cold mixture in carbon disulphide or in acetylene tetrachloride with aluminium chloride, were unsuccessful. However, when the mixture of *m*-cresol and phenylsuccinic anhydride was left with aluminium chloride for 24 hr. at room temperature or at 170° for 2 hr., it was converted into β-(2-hydroxy-4-methylbenzoyl)-α-phenylpropionic acid (IIIa; R″O·X = 2,4-HO·C_6H_3Me); the latter method gave a better yield. The position of succinoylation was established by methylating the product and oxidising the resulting methyl ether to a methoxyterephthalic acid. The exact structure of the methyl ether was confirmed by its identity with an authentic specimen prepared from the chalcone (VIIIb) according to scheme B.

When methyl *m*-tolyl ether was allowed to stand with aluminium chloride and phenylsuccinic anhydride at room temperature for 3 days, it gave β-(4-methoxy-2-methylbenzoyl)-α- or -β-phenylpropionic acid (VIc or d; R″O·X = 4,2-MeO·C_6H_3Me). Its structure was established by oxidation to 4-methoxyphthalic acid.

Scheme A


AlCl3
ArO·CO·CHR′·CHR·CO2H
ArÖ·CO·CHR′·CHR·CO2H
1
o-R″O·X·CO·CHR′·CHR·CO2H
(I) a: R = Ph, R′ = H
b: R = H, R′ = Ph
(II) a: R = Ph, R′ = H
R = H, R′ = Ph
(III) a: R = Ph, R′ = R″ = H
b: R = R″ = H, R′ = Ph
c: R = Ph, R′ = H, R″ = Me
d: R = H, R′ = Ph, R″ = Me
2
p-R″O·X·CO·CHR′·CHR·CO2H
[ArÖ·AlCl3− + +CO·CHR′·CHR·CO2H]
(VI) a: R = Ph, R′ = R″ = H
b: R = R″ = H, R′ = Ph
c: R = Ph, R′ = H, R″ = Me
d: R = H, R′ = Ph, R″ = Me
(V) Ar = Ph
(IV) a: R = Ph, R′ = H
b: R = H, R′ = Ph
p-C6H4Me·CO·CHR′·CHR·CO2H
(VII) a: R = Ph, R′ = H
b: R = H, R′ = Ph

Scheme B



The rearrangement of phenyl hydrogen phenylsuccinates appears to take place exclusively by an intermolecular mechanism according to scheme A (step 2). In presence of a solvent which is not susceptible to electrophilic attack, such as acetylene tetrachloride or nitrobenzene, the oxo-carbonium ion (IVa or b) attacks the *para*-position of the phenoxyaluminium chloride complex (V) to give acids (VIa and b; R″O·X = HO·C_6H_4). The intermolecular nature of the reaction was inferred from the facts that (i) no β-*o*-hydroxybenzoyl-α- or -β-phenylpropionic acid was formed, and (ii) the reaction in toluene gives nearly exclusively β-*p*-toluoyl-α- and -β-phenylpropionic acid, respectively.

That the *p*-tolyl esters (I) failed to give β-*p*-toluoyl-α- and -β-phenylpropionic acid when heated with aluminium chloride in toluene indicates that this rearrangement takes place intramolecularly, involving a π-complex [3] (cf. scheme A, step 1).

The reaction of phenylsuccinic anhydride with *m*-cresol appears to be a Fries rearrangement and not a Friedel–Crafts reaction, since the product is not the same as that from methyl *m*-tolyl ether. The reaction appears to proceed by the intermediate formation

[3] Dewar, "Electronic Theory of Organic Chemistry," Oxford, 1949, p. 229; Baddar and El-Assal, *J.*, 1950, 3606; Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56; Ralston, McCorkle, and Bauer, *J. Org. Chem.*, 1940, **5**, 645; Gershzon, *J. Gen. Chem.* (*U.S.S.R.*), 1943, **13**, 68; Cocker and Fateen, *J.*, 1951, 2632.

of β-*m*-tolyl hydrogen phenylsuccinate. A similar reaction took place with succinic anhydride.[1,4]

Experimental

β-(2-*Methoxy*-5-*methylbenzoyl*)-α-*phenylpropionitrile* (IXa).—A mixture of 2-methoxy-5-methylchalcone [5] (25 g.), 95% ethanol (5 ml.) and glacial acetic acid (6 g.) was warmed with stirring to 35°, and a 35% aqueous solution of potassium cyanide (37 ml.) was added during about 15 min. Stirring and warming were continued for 3 hr. After cooling, the precipitated nitrile was filtered off, and washed with cold 50% ethanol (8 ml.) and water until free from cyanide. The light yellow *nitrile* (26 g., 90%), crystallised from ethanol, had m. p. 103—104° (Found: C, 77·6; H, 6·1; N, 5·3. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1; N, 5·0%).

β-(2-*Methoxy*-5-*methylbenzoyl*)-α-*phenylpropionic Acid* (IIIc).—The solution of the nitrile (10 g.) in 60% alcoholic potassium hydroxide solution (20 ml.) was refluxed for 10 hr. The alcohol was evaporated under reduced pressure, then water was added. The obtained aqueous alkaline solution was extracted with ether, cooled in ice, then acidified with concentrated hydrochloric acid. β-(2-*Methoxy*-5-*methylbenzoyl*)-α-*phenylpropionic acid* (9 g., 80%), crystallised from benzene, had m. p. 173—174° (Found: C, 72·4; H, 6·1. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%).

The *methyl ester*, prepared in 75% yield by refluxing the acid (5 g.) with methyl sulphate (17 g.) and potassium carbonate (30 g.) in acetone (15 ml.) for 12 hr., had m. p. 67—68° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 72·7; H, 6·7. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·45%).

β-(2-*Methoxy*-4-*methylbenzoyl*)-α-*phenylpropionic Acid*.—Benzaldehyde (5·3 g., 0·05 mole) was added with stirring to a mixture of 2-methoxy-4-methylacetophenone [7] (8·2 g., 0·05 mole), ethanol (13 ml.), and 10% sodium hydroxide solution (20 ml.). The temperature was kept at 25—30° for 3 hr., then the whole was cooled in ice. The separated oil was extracted, washed,

Table 1.

Half-ester	M. p.	Solvent [1]	Yield (%) by method (*a*)	(*b*)	Formula	Found (%) C	H	Required (%) C	H
Ia; Ar = Ph	104—105°	C_6H_6–Pet.	19	11	$C_{16}H_{14}O_4$	70·5	5·2	71·1	5·2
Ib; Ar = Ph	130—131	C_6H_6	30	14		70·4	5·3		
Ia; Ar = *p*-Me·C_6H_4...	95—96	C_6H_6–Pet.	16	14	$C_{17}H_{16}O_4$	72·2	6·0	71·8	5·7
Ib; Ar = *p*-Me·C_6H_4...	128—129	C_6H_6	45	37		71·6	5·7		

[1] Pet. = light petroleum (b. p. 60—80°).

dried, and distilled to give 2-methoxy-4-methylchalcone (IXb) as a yellow liquid, b. p. 180—182°/1 mm. (10 g., 80% yield). It gave a deep red 2,4-*dinitrophenylhydrazone*, m. p. 204—205° (from acetic acid) (Found: C, 63·3; H, 4·6; N, 12·4; OMe, 7·8. $C_{23}H_{20}N_4O_5$ requires C, 63·9; H, 4·7; N, 12·9; OMe, 7·2%).

Glacial acetic acid (1 ml.) was added to a mixture of the chalcone (4 g.), ethanol (100 ml.), potassium cyanide (6 g.), and water (*ca.* 5 ml.). The mixture was kept at 70—80° for 50 hr. cooled, filtered, and evaporated under reduced pressure. The crude nitrile, a brown oil, was hydrolysed by refluxing concentrated hydrochloric acid (60 ml.) for 10 hr. The solid product was filtered off, dissolved in ether, washed, and extracted with concentrated sodium carbonate. Acidification of the alkaline solution gave β-(2-*methoxy*-4-*methylbenzoyl*)-α-*phenylpropionic acid* which, crystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 148—149° (3·5 g., 80% yield) (Found: C, 72·5; H, 6·1. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%).

Preparation of Aryl Hydrogen Phenylsuccinates (I).—(*a*) The phenol (0·1 mole) and phenylsuccinic anhydride (0·1 mole) were heated at 130—140° for 3 hr. The product was treated

[4] Raval, Bokil, and Nargund, *J. Univ. Bombay*, 1938, **7**, 184.
[5] Simonis and Lear, *Ber.*, 1926, **59**, 2908.
[7] Dilthey, Frode, and Koenen, *J. prakt. Chem.*, 1926, **114**, 153; Auwers, Lechner, and Bundesmann, *Ber.*, 1925, 58, 36.

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with ether, and the ethereal solution was extracted with ice-cold 5% sodium carbonate solution. (*b*) To a stirred, cooled mixture of the phenol (0·05 mole) and phenylsuccinic anhydride (0·05 mole) in carbon disulphide (75 ml.), anhydrous aluminium chloride (0·12 mole) was gradually added. Stirring was continued for a further 3 hr. The sticky brown mass was hydrolysed with ice and concentrated hydrochloric acid. Ether was then added and the ether–carbon disulphide layer was separated, washed with cold water, and extracted with cold concentrated sodium carbonate solution.

The ice-cold alkaline extract from (*a*) or (*b*) was acidified (at once, to avoid hydrolysis) and the oil was extracted with ether. Evaporation of the solvent gave a residue, which was extracted with hot benzene to remove any of the insoluble phenylsuccinic acid. Concentration of the filtrate precipitated the corresponding α-phenyl β-acid (Ib). Addition of light petroleum (b. p. 60—80°) to the mother liquor precipitated the β-phenyl α-acid (Ia). The results are summarised in Table 1.

Fries Rearrangement.—A stirred mixture of aryl hydrogen phenylsuccinate (0·011 mole) and solvent (0·115 mole) was treated gradually with aluminium chloride (0·022 mole) (Prolabo-Produite pour Laboratoires, Rhône Poulenc) at room temperature during 30 min. The temperature was kept thereat for another 30 min., then raised to 117° (boiling butan-1-ol bath) for a further 1·5 hr. The sticky dark brown mass obtained was hydrolysed with ice and dilute hydrochloric acid. The mixture was worked up by one of two procedures: (i) The solvent was removed in steam, and the precipitated dark solid residue was digested with the least possible amount of concentrated sodium carbonate solution. (ii) Ether was added and the ether solution was washed with water and extracted with sodium carbonate solution. The alkaline extract from (i) or (ii) was boiled to hydrolyse any unchanged ester (charcoal), filtered, and acidified with concentrated hydrochloric acid. In the case of *s*-tetrachloroethane or nitrobenzene, the precipitated acids were separated as recorded in Table 2. For the other solvent (toluene) the phenolic acids were separated from the non-phenolic acids by esterification with hydrogen chloride and ethanol. The alcohol was removed, and the product was extracted with ether and washed with sodium carbonate solution to remove unesterified acids, followed by sodium hydroxide solution to remove the phenolic esters (these were usually hydrolysed during extraction). Acidification of the sodium hydroxide solution precipitated the phenolic acid. The ester of the non-phenolic acid was hydrolysed with boiling 8% potassium hydroxide solution (3 hr.), and the acid (VII) was crystallised and identified by m. p. and mixed m. p. (cf. Table 2).

TABLE 2. *Yields (g.).*

	(Ia); Ar = Ph		(Ib); Ar = Ph		(Ia); Ar = *p*-C_6H_4Me		(Ib); Ar = *p*-C_6H_4Me	
Solvent	VIIa	VIa	VIIb	VIb	VIIa	IIIa	VIIb	IIIb
$C_2H_2Cl_4$	—	1·1 *	—	1·0 *	—	1·5 *	—	1·8 *
$PhNO_2$.....	—	0·75	—	0·70	—	1·1	—	1·2
PhMe	1·0 *	Traces	0·9 *	Traces	—	0·4 †	—	0·5 †

* See text. † Together with phenylsuccinic acid (0·8 g.).

β-(p-*Hydroxybenzoyl*)-α-*phenylpropionic acid*, crystallised from benzene–light petroleum (b. p. 60—80°), m. p. 204—205°, gave no colour with ferric chloride (Found: C, 71·1; H, 5·3. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%). This was methylated by methyl sulphate and potassium carbonate in acetone and the resulting methyl ether methyl ester was hydrolysed with 3% alcoholic potassium hydroxide to β-*p*-anisoyl-α-phenylpropionic acid, m. p. 149—150°, undepressed on admixture with an authentic specimen.[8]

β-(p-*Hydroxybenzoyl*)-β-*phenylpropionic acid*, crystallised from benzene, had m. p. 165—166° and gave no colour with ferric chloride (Found: C, 70·5; H, 5·3%). It gave β-*p*-anisoyl-β-phenylpropionic acid, m. p. 147—148°, undepressed on admixture with an authentic specimen.[8]

α-Phenyl-β-*p*-toluoylpropionic acid (from ether) had m. p. and mixed m. p. 153—154°.[9]

β-Phenyl-α-*p*-toluoylpropionic acid (from ether) had m. p. and mixed m. p. 156—157°.[9]

β-(2-*Hydroxy*-5-*methylbenzoyl*)-α-*phenylpropionic acid* (from benzene) had m. p. 130—131° and gave a violet colour with ferric chloride (Found: C, 71·9; H, 5·6. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%). Methyl β-(2-methoxy-5-methylbenzoyl)-α-phenylpropionate, prepared by

[8] Heller, *Ber.*, 1912, **45**, 418.
[9] Baddar, Fleifel, and Sherif, *J. Chem.* (*U.A.R.*), 1960, **3**, No. 1, 47.

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using methyl sulphate and potassium carbonate in acetone, had m. p. 167—168° [from benzene–light petroleum (b. p. 60—80°)], undepressed on admixture with an authentic specimen (see above). With toluene as solvent a considerable amount of phenylsuccinic acid was also obtained.

β-(2-*Hydroxy-5-methylbenzoyl*)-β-*phenylpropionic acid* (crystallised from benzene), m. p. 167—168°, gave a violet colour with ferric chloride (Found: C, 71·15; H, 5·8. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%). *Methyl* β-(2-*methoxy-5-methylbenzoyl*)-β-*phenylpropionate*, prepared as above, m. p. 59—60° [from light petroleum (b. p. <40°)], depressed on admixture with methyl β-(2-methoxy-5-methylbenzoyl)-α-phenylpropionate (above) (Found: C, 72·9; H, 6·2. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·45%). When toluene was the solvent a considerable amount of phenylsuccinic acid was also isolated.

Action of Aluminium Chloride on m-*Cresol and Phenylsuccinic Anhydride in* s-*Tetrachloroethane.*—(i) *At low temperature.* To an ice-cold mixture of *m*-cresol (9·2 g.) and phenylsuccinic anhydride (15 g.) in *s*-tetrachloroethane (130 g.), aluminium chloride (21 g.) was added in 3 lots. Stirring was continued for 4 hr. in ice, then the mixture was left overnight at room temperature. The product was worked up as usual, then treated with hot benzene to remove the insoluble phenylsuccinic acid (10·5 g.). On cooling, β-(2-*hydroxy*-4-*methylbenzoyl*)-α-*phenylpropionic acid* separated (9 g., 37%), having m. p. 172—173° (Found: C, 71·7; H, 5·65. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%). It gave a violet colour with alcoholic ferric chloride solution. (ii) *At high temperature.* The above experiment was repeated except that after addition of the 3 lots of aluminium chloride in the cold, the mixture was left for 0·5 hr. in ice and 1 hr. at room temperature, then heated for 2 hr. at 170—180°. β-(2-Hydroxy-4-methylbenzoyl)-α-phenylpropionic acid was obtained in 82% yield (20 g.).

The *methyl ether methyl ester*, prepared in quantitative yield by use of methyl sulphate and potassium carbonate in acetone (15 ml.), had m. p. 112—113° [from light petroleum (b. p. 60—80°)] (Found: C, 72·9; H, 6·2; OMe, 19·8. $C_{19}H_{20}O_4$ requires C, 73·0; H, 6·4; OMe, 19·9%).

β-(2-Methoxy-4-methylbenzoyl-α-phenylpropionic acid was obtained quantitatively by refluxing this ester (5 g.) in 3% alcoholic potassium hydroxide solution (100 ml.) for 2 hr., having m. p. and mixed m. p. 152—153° (from benzene).

Oxidation of the last acid (1 g.) by potassium permanganate (3 g.) in boiling 3% potassium hydroxide solution (40 ml.) for 2 hr. produced methoxyterephthalic acid (0·5 g.), m. p. 286—288° (from water, undepressed on admixture with an authentic specimen).[10]

Friedel–Crafts Reaction of Methyl m-*Tolyl Ether with Phenylsuccinic Anhydride.*—To a stirred ice-cold mixture of methyl *m*-tolyl ether (10·5 g.), phenylsuccinic anhydride (15 g.) and *s*-tetrachloroethane (130 g.), aluminium chloride (21 g.) was added in 3 lots. Stirring was continued for 4 hr. with ice-cooling, then the mixture was left at room temperature for 3 days with occasional stirring. The product was worked up as usual, then crystallised from benzene–light petroleum (b. p. 60—80°), to give β-(4-*methoxy*-2-*methylbenzoyl*)-α- or -β-*phenylpropionic acid* (18 g., 75%) m. p. 120—121° (Found: C, 72·2; H, 6·0. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%). Oxidation of the acid as above gave 4-methoxyphthalic acid, m. p. 170° (from water).

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[10] Duff, *J.*, 1941, 547.

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219. *Biosynthesis of* α-D-*Glucopyranosyl* D-*Galactofuranoside and Other* D-*Galactose-containing Saccharides by* Betacoccus arabinosaceous.

By E. J. Bourne, J. Hartigan, and H. Weigel.

B. arabinosaceous grown on a galactose–sucrose medium produces di- and oligo-saccharides. One of the disaccharides has been characterised as α-D-glucopyranosyl D-galactofuranoside. The glucose : galactose ratios of the oligosaccharides suggest that they are formed by successive addition of glucosyl units to a galactose-containing receptor.

It has been shown [1] that in cultures of *Betacoccus arabinosaceous* (Birmingham), containing sucrose as a substrate and isomaltose, maltose, methyl α-D-glucoside, or 3-*O*-methyl-D-glucose as receptor, oligosaccharides are formed by successive transfer of glucosyl units from the sucrose molecules to the receptor, with the formation of α-1,6-glycosidic linkages; with isomaltose and maltose the transfer was to the non-reducing moiety. In a previous paper [2] we established that the synthesis of the " branched " trisaccharide *O*-β-D-galactopyranosyl-(1 → 4)-*O*-[α-D-glucopyranosyl-(1 → 2)]-D-glucose in a lactose–sucrose medium proceeds by transfer of the glucosyl residue from sucrose to position 2 of the reducing unit of lactose. A similar trisaccharide, *O*-β-D-glucopyranosyl-(1 → 4)-*O*-[α-D-glucopyranosyl-(1 → 2)]-D-glucose is elaborated by the same organism when grown on a cellobiose–sucrose medium.[3] It was thought that the non-reducing moieties, β-D-galactosyl or β-D-glucosyl, in lactose and cellobiose did not provide suitable acceptor sites and thus tended to favour the transfer of the glucosyl residue from sucrose to the reducing moiety (αβ-D-glucose) of the receptor disaccharide. The present investigation, in which D-galactose was used as receptor, was of interest because the sugar was now present as *α- and β-D-galactose and, moreover, for the preferred C1-conformation, its 4-hydroxyl* group was axial, in contrast to the non-glucosidic hydroxyl groups of glucose.

A culture of *B. arabinosaceous*, grown on a D-galactose–sucrose medium, produced three disaccharides (A, B, and C) and two oligosaccharides (D and E). The sugars were isolated from the culture medium by fractionation on a charcoal–" Celite " column [4] and, when necessary, purified by paper chromatography. We now report the structure of disaccharide A and some properties of the other sugars.

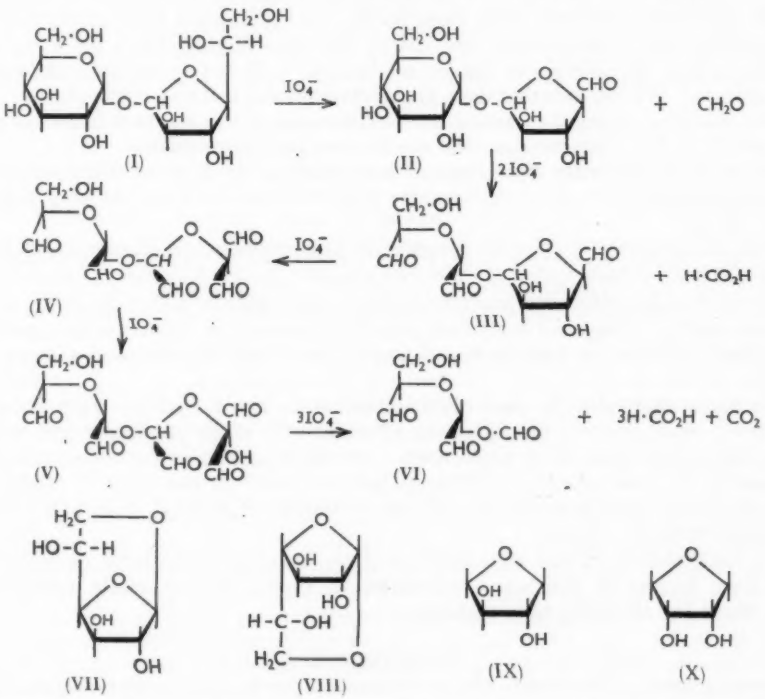
Chromatographically pure disaccharide A could be detected on paper chromatograms with acetone–silver nitrate–alcoholic sodium hydroxide,[5] but not with reagents specific for reducing sugars. Acid-hydrolysis yielded components identical with D-glucose and D-galactose on paper chromatography. Disaccharide A was immobile during electrophoresis in molybdate solution.[6] That it was a disaccharide was shown by the ratio of the constituent monosaccharides (glucose to galactose, 1 : 1·05) together with its rate of elution from a charcoal–" Celite " column and migration during chromatography.

Evidence for the non-reducing nature of disaccharide A was obtained by oxidation with alkaline hypoiodite [7] and Somogyi and Nelson's alkaline copper reagent,[8] and was confirmed when potassium borohydride failed to reduce it (paper chromatography of the product of an attempted reduction revealed a single component identical with disaccharide A; this component did not migrate during electrophoresis in molybdate solution, as would be expected of a disaccharide; [6] acid hydrolysis yielded only glucose and galactose).

[1] Bailey, Barker, Bourne, and Stacey, *J.*, 1957, 3530, 3536; Barker, Bourne, Grant, and Stacey, *J.*, 1958, 601.
[2] Bourne, Hartigan, and Weigel, *J.*, 1959, 2332.
[3] Bailey, Barker, Bourne, Grant, and Stacey, *J.*, 1958, 1895.
[4] (*a*) Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677; Lindberg and Wickberg, *Acta Chem. Scand.*, 1954, **8**, 569; (*b*) Barker, Bourne, and Theander, *J.*, 1955, 4276.
[5] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.
[6] Bourne, Hutson, and Weigel, *Chem. and Ind.*, 1959, 1047.
[7] Van der Plank, *Biochem. J.*, 1936, **30**, 457.
[8] Nelson, *J. Biol. Chem.*, 1944, **153**, 375; Somogyi, *ibid.*, 1945, **160**, 61.

Disaccharide A was hydrolysed by acid at a rate intermediate between those of αα-trehalose and sucrose and almost as fast as sucrose. This suggested that the glycosidic link between the D-glucosyl and the D-galactosyl unit was weakened by the presence of a furanosyl residue.

When treated with 5 mol. of periodate disaccharide A consumed in 800 min. 3·7 mol. of periodate and produced 1·45 mol. of formic acid and 0·83 mol. of formaldehyde. There was immediate consumption of 1 mol. of periodate followed by that of a further 2 mol. during the first 260 min. These values can be rationalised only when a D-glucopyranosyl D-galactofuranoside or a D-glucofuranosyl D-galactopyranoside structure is proposed for disaccharide A. Theoretically, complete oxidation of such a disaccharide (I) would consume 8 mol. of periodate and produce 4 mol. of formic acid, 1 mol. of formaldehyde, and 1 mol. of carbon dioxide (I—VI). The apparent discrepancy between the theoretical and the experimental values can be explained if the immediate oxidation stops with compound (III), whose further oxidation is then rate-determining. The resistance to periodate oxidation might be due to the formation of a cyclic semiacetal in the furanosyl



residue. Molecular models indicate that this is not so. On the other hand, 1,2-glycols derived from five-membered ring systems are not oxidised by periodate when the hydroxyl groups are securely locked in a *trans*-position, as in compounds (VII) [9] and (VIII): [10] L-threitan (IX), which has less securely locked *trans*-hydroxyl groups, reacts with periodate, but more slowly than the *cis*-compound erythritan (X); [11] further, Mitra and Perlin [12] have shown that the glucopyranosyl part of sucrose is more rapidly oxidised by periodate

[9] Dimler, Davis, and Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 1377.
[10] Alexander, Dimler, and Mehltretter, *J. Amer. Chem. Soc.*, 1951, **73**, 4658.
[11] Klosterman and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 5336.
[12] Mitra and Perlin, *Canad. J. Chem.*, 1959, **37**, 2047.

than the fructofuranosyl part. On the basis of these facts we believe that the rate-determining step is the further oxidation of (III), the adjacent hydroxyl groups of which are *trans* to one another.* Thus in the later stages of the oxidation of disaccharide (I) the consumption of $(3 + 5x)$ mol. of periodate should give rise to $(1 + 3x)$ mol. of formic acid. The consumption of 3·7 mol. of periodate should, on this theory, produce 1·42 mol. of formic acid and 1·0 mol. of formaldehyde. The experimental results are in good agreement with these values and so, we suggest, prove the pyranosyl furanoside structure of disaccharide A.

That the initial attack of periodate on disaccharide A removed a primary hydroxyl group as formaldehyde was shown when use of 1 mol. of periodate produced 0·58 mol. of formaldehyde. The oxidation product was reduced with potassium borohydride to an acid-labile disaccharide. Paper chromatography of the hydrolysate revealed the presence of components corresponding to D-glucose and L-arabinose. This showed that disaccharide A was a D-glucopyranosyl D-galactofuranoside. D-Galactopyranosyl D-glucofuranoside should have yielded D-galactose and D-xylose.

The configuration of the glycosidic links was investigated by treatment of disaccharide A with hydrolytic enzymes. The disaccharide was hydrolysed by a mixture of yeast α-glucosidase and α-galactosidase, but not by the same mixture when the α-glucosidase was inhibited by the addition of D-glucono-δ-lactone.[13] It was not hydrolysed by almond β-glucosidase. We conclude that the D-glucopyranosyl unit had an α-configuration. There was not sufficient evidence to assign the configuration of the D-galactofuranosyl unit as it is likely that the α-galactosidase was specific for galactopyranosides.

The evidence presented thus characterises disaccharide A as α-D-glucopyranosyl D-galactofuranoside. This is of considerable interest since the synthesis of a furanoside was involved.

Disaccharides B and C could be detected on paper chromatograms with acetone–silver nitrate–alcoholic sodium hydroxide and with reagents specific for reducing sugars. Acid-hydrolysis of each yielded components identical with D-glucose and D-galactose on paper chromatography. They had a glucosyl-galactose structure as reduction with potassium borohydride followed by hydrolysis and paper chromatography revealed glucose and a hexitol.

The chromatographically pure oligosaccharides D and E yielded, when completely hydrolysed, components with R_F values identical with those of glucose and galactose in the ratios of 2 : 1 and 3 : 1, respectively. Partial hydrolyses gave components corresponding to glucose, galactose, and isomaltose on paper chromatograms. These oligosaccharides may thus be formed by successive addition of glucosyl units to a galactose-containing receptor molecule.

It is thus established that α3-D-galactose serves as receptor of α-D-glucose units transferred from sucrose by *Betacoccus arabinosaceous*, though in view of the relatively low yields, much less efficiently than D-glucose.

Experimental

Chromatography.—The solvents used in chromatography were (*a*) butan-1-ol–ethanol–water (4 : 1 : 5) (organic phase); (*b*) butan-1-ol–benzene–pyridine–water (5 : 3 : 2 : 1); (*c*) butan-1-ol–pyridine–water–saturated aqueous boric acid (6 : 4 : 2 : 1).

Oligosaccharide Synthesis in a Galactose–Sucrose Medium.—An aqueous medium (150 ml.) containing yeast extract (1%), sodium ammonium hydrogen phosphate (0·5%), potassium dihydrogen phosphate (0·1%), hydrated magnesium sulphate (0·05%), and sucrose (2%) was adjusted to pH 7 with sodium hydroxide and sterilised, then inoculated with a strongly growing culture of *Betacoccus arabinosaceous* (Birmingham) and incubated at 25° for 60 hr.

* *Added*, 21.10.60: Since this paper was submitted, Kjølberg (*Acta Chem. Scand.*, 1960, **14**, 1118) has found that by lowering the temperature to 5° the periodate oxidation of methyl D-galactofuranosides and glucofuranosides can be confined to the 5,6-bond.

[13] Conchie and Levvy, *Biochem. J.*, 1957, **65**, 389.

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Galactose (20 g.), which had been purified by charcoal-column chromatography, was added and incubation continued for a further 5·5 days. Sterile 6% sucrose solutions (2·5 ml.) were added to the culture at intervals of 4 hr. throughout the first three days of the second incubation period.

The culture medium was adjusted to pH 7 and invertase (B.D.H. concentrate; 2 ml.) added to remove the residual sucrose. After incubation at room temperature for 1·5 hr. paper chromatography in solvent (*a*) and paper ionophoresis in borate buffer (pH 10) [14] revealed glucose, fructose, galactose, and oligosaccharides other than sucrose. The bacterial cells were removed by centrifugation (1 hr. at 5000 r.p.m.). After addition of ethanol (200 ml.) to precipitate dextran, the ethanol was removed from the supernatant liquid, and the residual solution was applied to a charcoal–" Celite " column [4] (30 × 8 cm.). The monosaccharides were eluted with water (4 l.), and the disaccharides with 5% aqueous ethanol (6 l.). Higher oligosaccharides were eluted with 10% (6 l.) and 15% aqueous ethanol (10 l.), respectively. Paper chromatography of the disaccharide fraction in solvent (*a*) showed the presence of one component with $R_{glucose}$ 0·46 and two components with $R_{glucose}$ *ca.* 0·38; ionophoresis in borate buffer (pH 10) revealed the presence of three components with M_G 0·54, 0·43, and 0·34, respectively.

Partial fractionation of the mixture of disaccharides was on a charcoal–" Celite " column (41 × 2·5 cm.) impregnated with 0·1M-borate buffer (pH 10), by elution with 0·1M-borate buffer (2·5 l.) and then with borate buffer containing 2·5% of ethanol (3 l.).[4b] Refractionation by paper chromatography in solvent (*a*) gave disaccharide A (47·6 mg.), B (32·7 mg.), and C (40·5 mg.).

Oligosaccharides D and E were obtained as chromatographically pure fractions when the charcoal–" Celite " column was eluted with 10% and 15% aqueous ethanol, respectively.

Properties of Disaccharide A.—(i) On a paper chromatogram irrigated with solvent (*a*) the disaccharide moved as single component with $R_{glucose}$ 0·46. Paper ionophoresis in borate buffer (pH 10) [14] again showed a single component with M_G 0·44. The disaccharide was revealed by acetone–silver nitrate–alcoholic sodium hydroxide [5] as a weak spot that appeared slowly and at the same rate as that due to αα-trehalose. It was not revealed with aniline hydrogen phthalate,[15] *p*-anisidine hydrochloride,[16] or triphenyltetrazolium chloride.[17]

The carbohydrate content, determined by the anthrone method,[18] was 96·1%.

(ii) Disaccharide A (*ca.* 1·5 mg.) was hydrolysed in 0·25N-sulphuric acid (2 ml.) at 100° *for 40 min. Paper chromatography of the hydrolysate in solvent (a) showed components* corresponding to glucose and galactose in equal quantities. The two components were isolated by paper chromatography. *Determination of the glucose and galactose* [8] *in aliquot parts of* the eluates revealed that they were present in the ratio of 1 : 1·05.

(iii) Disaccharide A (2·2 mg.), on oxidation with alkaline hypoiodite,[7] consumed iodine equivalent to 0·078 mg. of glucose or galactose (6·7% of the theoretical value for a disaccharide). When treated by the method of Somogyi and Nelson [8] disaccharide A had no reducing power.

(iv) Disaccharide A (2 mg.) was left in 0·05% potassium borohydride solution (0·5 ml.) overnight at room temperature. The solution was de-ionised by Amberlite resin IR-120 (H^+), then evaporated to dryness and distilled with dry methanol (3 × 2 ml.). Paper chromatography of the residue in solvents (*a*) and (*b*) revealed a single component identical with disaccharide A, immobile during electrophoresis in molybdate solution.[6]

This residue was hydrolysed with 1·5N-sulphuric acid at 100° for 4 hr. Paper chromatography of the de-ionised hydrolysate in solvent (*c*) revealed components corresponding to glucose and galactose.

(v) Disaccharide A (0·4 mg.), αα-trehalose (*ca.* 2 mg.), and sucrose (*ca.* 2 mg.) were separately hydrolysed with 0·25N-sulphuric acid (0·25 ml. and 1 ml.) at 100° for 15 min. Paper chromatography of the de-ionised hydrolysates showed that disaccharide A had been almost completely hydrolysed (*ca.* 90%) to glucose and galactose. Sucrose had been completely hydrolysed to glucose and fructose. Only a trace of glucose (<10%) was liberated from αα-trehalose.

(vi) *Periodate oxidation.* Treatment of disaccharide A (10·3 mg.) with 0·015M-sodium

[14] Foster, *J.*, 1953, 982.
[15] Partridge, *Nature*, 1949, **164**, 443.
[16] Hough, Jones, and Wadman, *J.*, 1950, 1702.
[17] Feingold, Avigad, and Hestrin, *Biochem. J.*, 1956, **64**, 351.
[18] Bailey, *Biochem. J.*, 1958, **68**, 669.

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metaperiodate (10 ml.) in the dark at room temperature gave the following results. The periodate consumption, expressed in moles per mole of disaccharide A, was 1·2 (10 min.), 2·5 (150 min.), 2·9 (260 min.), 3·3 (480 min.), 3·5 (700 min.), 3·7 (800 min.). After 24 hr. all the periodate had been reduced. After 800 min. 1·45 moles of formic acid and 0·83 mole of formaldehyde were produced per mole of disaccharide A.

On treatment of αα-trehalose under the same conditions, the periodate consumption was 0·7 (10 min.), 3·2 (240 min.), 3·5 (360 min.), 3·6 (540 min.), 3·6 (1380 min.). After 540 min. 1·4 moles of formic acid were produced per mole of αα-trehalose. No formaldehyde was produced.

When the disaccharide A (0·34 mg.), dissolved in water (10 ml.), was treated with 0·001M-sodium metaperiodate (1 ml.) the formaldehyde produced (mole per mole) was 0·36 (7 hr.), 0·58 (23 hr.), 0·58 (48 hr.). The solution was then de-ionised with Permutit " Biodeminrolit " resin, pretreated with carbon dioxide. Potassium borohydride (50 mg.) in water (1 ml.) was added and the solution left overnight at room temperature, de-ionised by Amberlite resin IR-120 (H^+), and evaporated to dryness. The residue was distilled with dry methanol (3 × 2 ml.), then treated with 0·25N-sulphuric acid (5 ml.) at 100° for 15 min. The de-ionised hydrolysate was analysed by paper chromatography in solvent (*b*) which revealed components corresponding to D-glucose and L-arabinose, but not to galactose and xylose. They were detected with acetone–silver nitrate–alcoholic sodium hydroxide [5] and *p*-anisidine hydrochloride.[16] The latter reagent gave a pink stain, typical of pentoses with the component corresponding to L-arabinose and a yellowish stain with that corresponding to D-glucose.

(vii) A solution of disaccharide A (1%) was sealed in a capillary tube with an equal volume of almond β-glycosidase solution.[19] Paper chromatography of the digest after incubation at 35° for 72 hr. showed that no hydrolysis had occurred. Under the same conditions cellobiose was completely hydrolysed, lactose partially hydrolysed, and maltose was not hydrolysed. A 1% solution of disaccharide A was sealed in a capillary tube with an equal volume of yeast α-glucosidase [20] solution. Paper chromatography of the digest after incubation at 26° for 48 hr. revealed components corresponding to glucose and galactose. Under the same conditions, maltose was completely hydrolysed and melibiose partially hydrolysed. Lactose and cellobiose were not hydrolysed. A 1% solution of disaccharide A was sealed in a capillary tube with an equal volume of yeast α-glycosidase [20] solution, to which D-glucono-δ-lactone (2%) had been added: [19] paper chromatography of the digest after incubation at 26° for 72 hr. revealed absence of hydrolysis. Under the same conditions maltose was not hydrolysed and melibiose was partially hydrolysed.

Investigation of Disaccharides B and C.—(i) On a paper chromatogram irrigated with solvent (*a*) the disaccharides B and C moved with $R_{glucose}$ 0·39 and 0·36, and M_G 0·60 and 0·34, respectively. Disaccharide B was probably contaminated with a trace of leucrose. For detection see p. 1090.

(ii) Materials B (1 mg.) and C (1 mg.) in N-sulphuric acid at 100° for 4 hr. gave glucose and galactose (identified by paper chromatography). Sugar B also gave a trace of fructose.

(iii) Disaccharides B (2 mg.) and C (2 mg.) were separately treated with potassium borohydride (as above). The reduction products were hydrolysed with 1·5N-sulphuric acid at 100° for 4 hr. Paper chromatography of the hydrolysates in solvent (*c*) revealed components corresponding to glucose and a hexitol, but not galactose.

Investigation of Oligosaccharides D and E.—Chromatographically pure oligosaccharides D and E [$R_{glucose}$ 0·16 and 0·18, respectively, in solvent (*a*)] were separately hydrolysed in 1·5N-sulphuric acid at 100° for 4 hr. Paper chromatography then revealed components corresponding to glucose and galactose in the ratios of 2 : 1 and 3 : 1, respectively. Partial hydrolysis of D and E in N-sulphuric acid at 90° gave glucose, galactose, and isomaltose on paper chromatography.

The authors are indebted to Dr. R. W. Bailey for helpful discussions and the Department of Scientific and Industrial Research, the Royal Society, and the Central Research Funds Committee of the University of London, for financial assistance.

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[19] Onslow, " Practical Plant Biochemistry," Cambridge Univ. Press, 1929.
[20] Krieble, Skau, and Lovering, *J. Amer. Chem. Soc.*, 1927, **49**, 1728.

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220. *Influence of Pressure on the Hammett Reaction Constant: Dissociation of Benzoic Acids and Phenylacetic Acids.*

By A. Fischer, B. R. Mann, and J. Vaughan.

The thermodynamic pK values, in water at 25°, of a number of substituted benzoic and phenylacetic acids have been measured over the pressure range 1—3000 bars. For each series the Hammett reaction constant ρ decreases with increase in pressure, a result expected for this type of reaction. It is clear also that, for a given reaction series at a given pressure, a plot of ΔV against σ (substituent constant) reveals any dependence of ρ on pressure.

The probable effect of pressure on the Hammett reaction constant ρ has been discussed, and predictions have been made for heterolytic and homolytic reactions in polar and non-polar solvents.[1] For some sets of conditions, the conclusion reached was that ρ should be unaltered by pressure changes. This should not be so, however, for a reaction producing ions in a polar solvent, a case for which it was predicted that an increase in pressure should result in a decrease in the magnitude of ρ. At present there are no results available for full reaction series studied at a variety of pressures, and the only relevant data which can be used are pK values for benzoic and *m*-nitrobenzoic acids.[2] From this limited information it was tentatively concluded that ρ for the benzoic acid series is, in fact, influenced by pressure and diminishes with increasing pressure. We now report the thermodynamic pK values, in water, of benzoic acid and *m*-fluoro-, *p*-fluoro-, *m*-methoxy-, *p*-methoxy-, *m*-nitro-, and *p*-nitro-benzoic acids at 25° and at pressures from 1 to 3000 bars. The phenylacetic acid series, with *m*-chloro-, *p*-chloro-, *m*-fluoro-, *p*-fluoro-, *p*-methoxy-, *m*-nitro-, *p*-nitro-, and *p*-methyl substituents, was similarly examined.

Experimental

Materials.—"AnalaR" potassium chloride was dried at 120° for 2 hr. and "AnalaR" hydrochloric acid was standardised against recrystallised borax. Of the organic acids, phenylacetic acid, *p*-methyl-, *m*-fluoro- and *p*-fluoro-phenylacetic acids were recrystallised from heptane and all other acids from ethanol–water. All m. p.s were within a degree of the accepted values. *m*-Fluorophenylacetic acid was prepared by refluxing the nitrile (40·2 g.) with water (40 ml.), sulphuric acid (40 ml.), and acetic acid (40 ml.) for 2¼ hr. The mixture was poured on cracked ice (250 g.), and the crude acid, after filtration, was dissolved in sodium carbonate solution (3%; 600 ml.). After extraction with chloroform (100 ml.) and ether (100 ml.), the solution was acidified with concentrated hydrochloric acid, and the liberated *m*-fluorophenylacetic acid was extracted with ether (3 × 50 ml.). Ether was removed and the acid distilled at 100—120°/0·5 mm. and crystallised from heptane (150 ml.), giving white crystals (27 g.), m. p. 44·5—45·5° (Found: C, 62·6; H, 4·7. $C_8H_7FO_2$ requires C, 62·6; H, 4·55%). Standard solutions of the organic acids were made up by weight, each solution usually being used for one run only, although in a few instances standard solutions were progressively diluted for a series of runs. Water free from carbon dioxide was used for all solutions. Solutions of potassium salts were prepared by adding the calculated volume of standard, carbonate-free potassium hydroxide solution to the weighed acid. Checks with a pH meter confirmed that all salt solutions had pH values within the range 7·5—8·5.

Apparatus.—Pressures were generated by means of a simple hand-operated hydraulic intensifier and the conductance cell was enclosed in a stainless steel bomb [3] sealed by an O-ring.[4] The conductance cell was one designed after consultation with Dr. A. J. Ellis. The glass cell (*ca.* 2 ml. capacity) was pear-shaped, the narrow end having a small orifice (*ca.* 0·25 mm. diam.) at its extremity. This end of the cell was ground to fit a B14 socket. To the neck of the

[1] Ellis, Fyfe, Rutherford, Fischer, and Vaughan, *J. Chem. Phys.*, 1959, **31**, 176.
[2] See Clark and Ellis, *J.*, 1960, 247, for full details of these measurements.
[3] Ellis, *J.*, 1959, 3689.
[4] Gugan, *J. Sci. Instr.*, 1956, **33**, 160.

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ground-glass socket was attached a flexible Teflon bag of capacity similar to that of the cell. The electrodes were small platinum balls and the links to the external circuit were of fine platinum wire passing through the glass wall of the cell. Earlier difficulties (at high pressures) caused by cracking at the platinum-glass seals were not experienced when the diameter of the wire was reduced to 0·04 mm. When the whole unit (cell plus bag) was filled with solution, and suspended in the steel bomb, the cell contents were isolated from the hydraulic fluid. The flexible bag still allowed pressure to be transmitted to the cell liquid *via* the small orifice. With this unit the variation with pressure of the cell constant depended only upon the compressibilities of glass and platinum, and this small variation could readily be calculated from Bridgman's figures.[5] The cell constant at 1 bar was 0·639 ± 0·005 cm.$^{-1}$.

Pressures were measured with a Bourdon gauge calibrated with a Harwood standard manganin coil resistance. In practice, accuracy was limited by dial readings but recorded pressures were considered accurate to within 0·5%. The conductivity bridge has been described previously,[6] and its high sensitivity proved of great advantage when studying the organic acids of low solubility.

Dissociation Constants.—The pK values were obtained by using the general approach due to Davies [7a] and MacInnes.[7b] The thermodynamic dissociation constant for the ionisation of an acid HA is given by

$$K_a = a_{H^+} \cdot a_{A^-}/a_{HA} = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}} \cdot \frac{f_{H^+} \cdot f_{A^-}}{f_{HA}}$$

The activity of undissociated molecules is taken as unity and it is also assumed that $f_{H^+} = f_{A^-} = f_{\pm}$. Since $c_{H^+} = c_{A^-} = c_i$, $K = f_{\pm}^2 c_i^2/c_{HA}$.

If α is the degree of dissociation and m is the original molal concentration of the acid solution, then $c_i = \alpha m$ and $c_{HA} = m(1 - \alpha)$. Then $K_a = f_{\pm}^2 \alpha^2 m/(1 - \alpha)$.

If λ is the molal conductance of the acid solution and λ' is the molal conductance of the constituent ions at the ionic concentration of the acid solution, then $\alpha = \lambda/\lambda'$. α can be obtained by a series of successive approximations (see example below).

In water, and at the concentrations used, the molal activity coefficient $\gamma_{\pm}$ = the molar activity coefficient $f_{\pm}$, which can be obtained at all concentrations and pressures from the Debye–Hückel equation expressed as:

$$-\log f_{\pm} = \{1{\cdot}8123 \times 10^6 (DT)^{-3/2} c^{\frac{1}{2}}\}/\{1 + 50{\cdot}29 \times 10^8 (DT)^{-\frac{1}{2}} a c^{\frac{1}{2}}\}$$

In this expression, T is the absolute temperature, c is the ionic concentration, and a is the ionic radius, taken as 5×10^{-8} cm. D is the dielectric constant, and its pressure dependence can be found by using Owen and Brinkley's formula.[8]

The following example illustrates the general procedure followed for the determination of K_a at a specific pressure: m-Chlorophenylacetic acid, m = 0·001787 at 1000 bars. Resistance of acid solution at 1000 bars = 3650·85 ohms ± 0·1%. Resistance corrected for water blank = 3689·00 ohms ± 0·2%. $\lambda = (1000 \times 0{\cdot}639)/(3689{\cdot}00 \times 0{\cdot}001787) = 96{\cdot}98$ ohm^{-1} cm.^{2} ± 0·7%.

Conductance of constituent ions at infinite dilution, $\lambda_0 = 404{\cdot}3$ ohm^{-1} cm.^{2} ± 0·2%. α_1, the first of a series of approximations to α, is given by $\lambda/\lambda_0 = 0{\cdot}240$. Thus c_1, the first approximation to the ionic concentration, = 0·000429 g.-ion/1000 g.

By interpolation in the plots of (concentration)$^{\frac{1}{2}}$ against the conductances of hydrochloric acid, of potassium chloride, and of potassium m-chlorophenylacetate, λ is obtained for these electrolytes at 1 bar at the above concentration. For each of these electrolytes, the mean pressure variation is given in Table 1. The term " λ × mean pressure variation at 1000 bars " is evaluated for each of the three electrolytes and the sum of these terms gives λ'_1, the first approximation to λ'.

$$\lambda'_1 = 414{\cdot}60. \quad \alpha_2 = \lambda/\lambda'_1 = 0{\cdot}234$$

[5] Bridgman, (*a*) *Amer. J. Sci.*, 1925, **10**, 359; (*b*) *Proc. Amer. Acad.*, 1923, **58**, 166.
[6] Fischer, Murdoch, Packer, Topsom, and Vaughan, *J.*, 1957, 4358.
[7a] Davies, *J. Phys. Chem.*, 1925, **29**, 977.
[7b] MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068.
[8] Hamann, " Physico-chemical effects of pressure," Butterworths, London, 1957, p. 104.

Thus $c_2 = 0{\cdot}000418$ g. ion/1000 g.; $\lambda'_2 = 414{\cdot}15$;

$$\alpha_3 = 0{\cdot}234 \pm 0{\cdot}9\%; \text{ and } 1 - \alpha_3 = 0{\cdot}766.$$

From the Debye–Hückel approximation, $-\log \gamma_{\pm} = 0{\cdot}00925$. Thus $K_a = \gamma_{\pm}^2\alpha^2 m/(1-\alpha) = 1{\cdot}224 \times 10^{-4} \pm 2{\cdot}7\%$, and the p$K$ value is $3{\cdot}912 \pm 0{\cdot}01$.

Results.—Table 1 gives, for general interest, the measured variation of conductance with pressure for the strong electrolytes relevant to the present work. In this Table, λ_0 = molal conductance at infinite dilution and λ_P/λ_1, is the ratio of molal conductances at pressures P and 1 bar. An omission from the Table is potassium *p*-nitrophenylacetate, which was not sufficiently soluble to allow conductance measurements to be made. For the calculation of the pK of the acid, conductance values for this salt were taken as approximately the mean values for the other phenylacetates.

In Tables 2 and 3 are the mean derived pK values for benzoic acids and phenylacetic acids,

TABLE 1. *Conductances of strong electrolytes.*

P (bars)	1	500	1000	1500	2000	2500	3000
	λ_0	λ_P/λ_1					
Hydrochloric acid	426·16	1·051	1·093	1·127	1·155	1·177	1·195
Potassium chloride	149·86	1·034	1·056	1·068	1·074	1·073	1·067
Potassium benzoates:							
Unsubstituted	115·0	1·022	1·034	1·036	1·035	1·027	1·016
p-nitro-	106·2	1·023	1·037	1·041	1·041	1·036	1·027
p-methoxy-	108·2	1·024	1·037	1·041	1·039	1·032	1·021
m-methoxy-	105·4	1·023	1·035	1·038	1·036	1·028	1·016
m-fluoro-	110·4	1·022	1·034	1·038	1·035	1·026	1·015
m-nitro-	109·9	1·022	1·035	1·037	1·036	1·028	1·017
p-fluoro-	108·4	1·023	1·035	1·039	1·037	1·028	1·017
Potassium phenylacetates:							
Unsubstituted	107·4		1·038		1·037		1·018
m-nitro-	106·7		1·034		1·034		1·014
m-chloro-	103·5		1·035		1·036		1·016
p-chloro-	108·7		1·036		1·038		1·019
p-methoxy-	107·4		1·036		1·040		1·021
p-methyl-	106·6		1·037		1·042		1·024
m-fluoro-	109·2		1·037		1·041		1·024
p-fluoro-	109·9		1·036		1·037		1·017

TABLE 2. *Benzoic acids, mean p*K *values.*

P (bars)	1	500	1000	1500	2000	2500	3000
Substituent:							
H	4·205	4·107	4·021	3·943	3·865	3·795	3·726
$n = 3$, s	0·003	0·003	0·003	0·003	0·003	0·003	0·004
m-F	3·862	3·776	3·694	3·620	3·546	3·477	3·412
$n = 4$, s	0·006	0·006	0·005	0·007	0·007	0·007	0·007
p-F	4·153	4·061	3·976	3·900	3·822	3·753	3·687
$n = 4$, s	0·004	0·003	0·003	0·003	0·003	0·004	0·004
m-NO_2	3·473	3·397	3·328	3·258	3·192	3·130	3·070
$n = 4$, s	0·006	0·006	0·007	0·007	0·007	0·007	0·008
p-NO_2	3·422	3·347	3·275	3·209	3·142	3·081	3·022
$n = 4$, s	0·014	0·014	0·016	0·017	0·018	0·020	0·022
m-OMe	4·086	3·995	3·911	3·834	3·759	3·691	3·625
$n = 3$, s	0·006	0·008	0·008	0·007	0·007	0·008	0·007
p-OMe	4·511	4·411	4·320	4·237	4·156	4·083	4·013
$n = 5$, s	0·005	0·005	0·005	0·005	0·005	0·006	0·007

at 25° ± 0·01°, over the pressure range 1—3000 bars. The standard deviation (s) with the number of pK determinations (n) are also given for each acid. In Table 4 are values, for all acids, of ΔV_1, the volume change on ionisation at 1 bar (calculated from the variation of K with P).

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TABLE 3. *Phenylacetic acids, mean pK values.*

P (bars)	1	1000	2000	3000
Substituent:				
H	4·311	4·095	3·917	3·762
$n = 4$, s	0·005	0·005	0·005	0·009
p-Me	4·361	4·147	3·965	3·808
$n = 5$, s	0·003	0·004	0·003	0·004
m-NO_2	3·953	3·766	3·605	3·466
$n = 6$, s	0·015	0·016	0·016	0·017
p-NO_2	3·924	3·740	3·580	3·437
$n = 3$, s	0·013	0·009	0·016	0·017
p-Cl	4·177	3·971	3·799	3·649
$n = 5$, s	0·006	0·004	0·003	0·005
p-OMe	4·356	4·146	3·967	3·811
$n = 5$, s	0·003	0·002	0·003	0·004
m-Cl	4·110	3·911	3·738	3·585
$n = 5$, s	0·013	0·016	0·016	0·013
m-F	4·130	3·927	3·754	3·603
$n = 5$, s	0·004	0·006	0·006	0·006
p-F	4·218	4·007	3·829	3·676
$n = 5$, s	0·003	0·003	0·004	0·003

TABLE 4. *ΔV values (c.c. mole^{-1}) at one bar.*

(*a*) Benzoic acids

Substituent	H	*m*-F	*p*-F	*m*-NO_2	*p*-NO_2	*m*-OMe	*p*-OMe
$-\Delta V_1$	11·09	9·85	10·47	8·84	8·56	10·30	11·32

(*b*) Phenylacetic acids

Substituent	H	*m*-NO_2	*p*-NO_2	*m*-Cl	*p*-Cl	*m*-F	*p*-F	*p*-Me	*p*-OMe
$-\Delta V_1$	12·73	11·09	10·92	11·77	12·16	11·99	12·44	12·61	12·39

DISCUSSION

pK and V Values.—The dissociation constants, at atmospheric pressure, are in good agreement with those recorded by Dippy and his co-workers.[9] The ΔV_1 values lie within the same range as those found by Hamann and Strauss for formic, acetic, and propionic acids (−8·8, −12·2, and −12·9 cm.^{3} mole^{-1}, respectively). Clark and Ellis [2] have recently reported ΔV_1 values for three of the acids studied in the present work. They are benzoic ($\Delta V_1 = -10{\cdot}6$ cm.^{3} mole^{-1}), *m*-nitrobenzoic (−8·7), and *p*-nitrobenzoic (−9·1) acids.

Hammett Plots.—In obtaining the reaction constant (ρ) from the Hammett equation, all substituent constants (σ) used for the benzoic acid series were those recommended by McDaniel and Brown.[10] Jaffé's method [11] was followed and the relevant data are in Table 5(*a*). The probable error in ρ is ±0·01. Briegleb and Bieber,[12] who studied seven benzoic acids at 25° and 1 bar, obtained $\rho = 0{\cdot}958$, with $r = 0{\cdot}996$ and $s = 0{\cdot}027$.

In the phenylacetic acids, resonance involving substituent and carboxyl side-chain is inhibited by the methylene group. Wepster's σ_N values [13] were used in calculations of ρ. At 1 bar, all substituents were included except the *p*-fluoro-substituent, which was fitted to the line to obtain $\sigma_N = 0{\cdot}167$. This value was used in subsequent determinations of ρ at 1000, 2000, and 3000 bars. Results are in Table 5(*b*), and the probable error in ρ values is ±0·006. The ρ value from Dippy's results at 25° is 0·519, with $r = 0{\cdot}988$ and $s = 0{\cdot}026$ for 12 substituents.

Variation of ρ with Pressure.—It is clear from Table 5 that, in accord with prediction,

[9] Dippy and Lewis, *J.*, 1936, 644; Dippy and Page, *J.*, 1938, 357; Dippy and Williams, *J.*, 1934, 161; Dippy and Williams, *J.*, 1924, 1888.
[10] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.
[11] Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[12] Briegleb and Bieber, *Z. Electrochem.*, 1951, **55**, 250.
[13] Van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

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ρ diminishes with increase in pressure. It may be assumed that, as P increases and the solvent becomes more compressed, the contraction produced on ionisation becomes smaller.

TABLE 5. *Application of Hammett equation.*

(*a*) Benzoic acids ($n = 7$)

P (bars)	ρ	r	s	s_ρ	pK_0 (calc.)
1	1·039	1·000	0·013	0·014	4·217
500	1·013	1·000	0·013	0·014	4·122
1000	0·996	1·000	0·013	0·014	4·036
1500	0·979	1·000	0·013	0·014	3·957
2000	0·965	1·000	0·013	0·014	3·880
2500	0·954	0·999	0·014	0·015	3·810
3000	0·943	0·999	0·014	0·015	3·742

(*b*) Phenylacetic acids

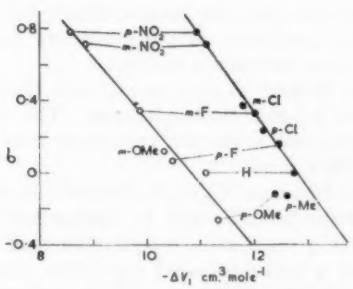
P (bars)	ρ	r	s	s_ρ	n	pK_0 (calc.)
1	0·491	0·999	0·007	0·008	8	4·300
1000	0·457	0·999	0·008	0·009	9	4·088
2000	0·434	0·998	0·009	0·010	9	3·909
3000	0·417	0·998	0·009	0·010	9	3·754

Hence $-\Delta V$ and, consequently, $|\Delta\Delta V|$ decrease (*e.g.*, see Table 6), and, from $\partial\rho/\partial P = -\Delta\Delta V/2{\cdot}303\boldsymbol{R}T\sigma$, $-\partial\rho/\partial P$ decreases also. At sufficiently high pressures, $\Delta\Delta V$ should approach zero and ρ should approach a constant value.

TABLE 6. *Variation of* ΔVp *with pressure for* p-*methoxybenzoic acid.*

P (bars)	1	500	1000	1500	2000	2500	3000
$-\Delta V$	11·32	10·25	9·35	9·12	8·22	7·89	7·66

It is to be noted that, for a given reaction, values of ΔV can be used to check whether or not ρ depends on P. From the above equation, since $\Delta\Delta V/\sigma$ is independent of σ, if ρ is a function of P, then ΔV is a linear function of σ at constant (T, P). If ρ is independent of P, then $\Delta\Delta V/\sigma = 0$ and ΔV is independent of σ. Thus, at any given pressure, a plot



The variation of ΔV_1 with Hammett substituent constant.

○ *Benzoic acids.* ● *Phenylacetic acids.*

of ΔV against σ should be linear, and a slope other than zero reveals a dependence of ρ on P. Zero slope indicates that ρ remains constant at different pressures. The plots of ΔV_1 against σ for benzoic and phenylacetic acids are given in the Figure.

A Research Fund Fellowship of the University of New Zealand (to B. R. M.) is gratefully acknowledged.

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[*Received, May 2nd,* 1960.]

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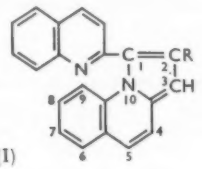
221. *The Quinoline Series. Part II.*[1] *The Reaction between Quinaldine and Sulphuric Acid.*

By S. Skidmore and E. Tidd.

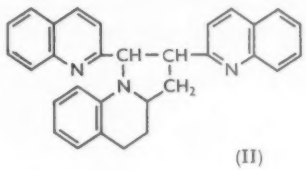
By reaction between quinaldine and either sulphuric acid or sulphur a pyrroloquinoline (I; R = 2-quinolyl) has been obtained. Evidence is presented in support of this structure and a possible general synthesis of pyrrolo[1,2-*a*]quinolines by cyclisation of quinolylpropanes is described.

The preparation and reactions of intermediates in the synthesis have been re-examined.

In an earlier paper [1] we described the acid-catalysed additions of quinaldine and lepidine to activated olefinic systems. In the addition of quinaldine to ethyl cinnamate with sulphuric acid as catalyst it was evident that other reactions as well as addition were occurring. These have now been shown to involve only the quinaldine and the sulphuric acid. From the reaction mixture, three bases have been isolated. One has been identified as 1,2-di-2′-quinolylethane, and the second is considered to be a pyrroloquinoline (benzopyrrocoline) (I; R = 2-quinolyl), but the nature of the third is unknown.



(I)



(II)

The identity of the 1,2-di-2′-quinolylethane was confirmed by an independent synthesis from ω-bromoquinaldine and sodium in xylene as described by Hammick *et al.*[2] Only small amounts of the compound were obtained in this synthesis and it is not considered to be a satisfactory method.

Since sulphur was formed during the quinaldine–sulphuric acid reaction the effect of heating quinaldine with sulphur was examined and the product shown to contain the three bases previously isolated.

von Miller,[3] Walker *et al.*,[4] and Hammick *et al.*,[5] treating quinaldine with sulphur, isolated 1,2-di-2′-quinolylethane. The nature of the base which we consider to be a pyrroloquinoline has not previously been elucidated although its formation was recorded by Walker *et al.*[4]

The free base, $C_{30}H_{19}N_3$, is pale yellow whereas its quaternary salts are red. It forms a monomethiodide, and a monopicrate. Oxidation with potassium permanganate in pyridine gives 2 mols. of quinaldic acid. Hydrogenation with Raney nickel in ethanol yielded a cream-coloured crystalline compound, $C_{30}H_{25}N_3$, which formed a pale yellow hydrochloride. Structure (II) is proposed for this compound since hydrogenation of benzene and quinoline systems is known to require more vigorous conditions than those employed here.

The ultraviolet absorption spectrum of the free base shows maxima at 270 (strong), 326 (weak), and 352 (weak).

After reaction between 2-picoline and sulphur, Emmert and Groll [6] isolated a disulphide

[1] Part I, Skidmore and Tidd, *J.*, 1959, 1641.
[2] Hammick, Brown, and Thewlis, *J.*, 1951, 1145.
[3] von Miller, *Ber.*, 1888, **21**, 1828.
[4] Walker, Baldwin, Thayer, and Corson, *J. Org. Chem.*, 1951, **16**, 1805.
[5] Hammick, Lammiman, Morgan, and Roe, *J.*, 1955, 2436.
[6] Emmert and Groll, *Chem. Ber.*, 1953, **86**, 205.

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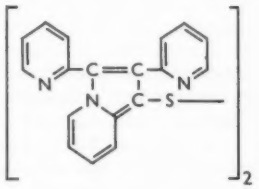
(III) which they reduced to the base (IV). The pyrroloquinoline now isolated from the corresponding reaction of quinaldine appears to be the quinoline analogue of (IV).

Thayer and Corson [7] have shown that 1,2-di-4′- and 1,2-di-2′-pyridylethylene are formed by reaction of sulphur with 4- and 2-picoline respectively. Although 1,2-di-2′-quinolylethylene has never been isolated from the quinaldine–sulphur reaction it is likely to be formed by dehydrogenation of the diquinolylethane present. In the presence of acids, addition of quinaldine to the diquinolylethylene could occur and the resulting triquinolylpropane (V; R = 2-quinolyl) could undergo dehydrogenation through its tautomeric form (VI). Such a sequence of reactions would account for the absence of a pyrrocoline derivative in the products of reaction of sulphur with 4-picoline or lepidine since a methylene group in the 2-position of the pyridine ring is essential for cyclisation. A synthesis along these lines was successful. 1,2-Di-2′-quinolylethane was obtained from quinaldine and sulphur, and was dehydrogenated with selenium dioxide to the olefin. When quinaldine hydrochloride was used as catalyst, quinaldine was added to the diquinolylethylene to yield 1,2,3-triquinolylpropane, and heating this with sulphur gave the pyrroloquinoline (I; R = 2-quinolyl). Similarly 2-phenyl-1,3-di-2′-quinolylpropane (V; R = Ph) on dehydrogenation by sulphur gave the pyrroloquinoline (I; R = Ph). Both pyrroloquinolines gave red quaternary salts and they had similar ultraviolet absorption spectra.



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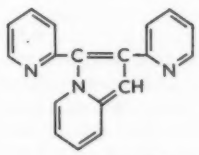

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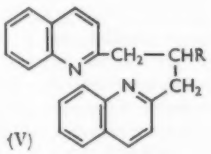

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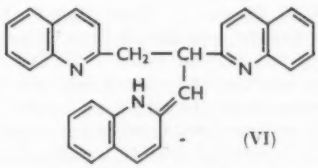

(VI)

A similar cyclisation was observed by Battersby and Edwards [8] when they oxidised the bisdihydroisoquinolylpropane (VII) with mercuric acetate to the colourless base (VIII) which formed a red hydrobromide. When we used mercuric acetate to oxidise 2-phenyl-1,3-di-2′-quinolylpropane the pyrroloquinoline (I; R = Ph) was again obtained, but only in low yield.

During this work problems arose in the preparation of 1,2-di-2′-quinolyl-ethanol and -ethylene. The diquinolylethanol prepared by Kaplan and Lindwall's method [9] contained 1,2-di-2′-quinolylethane-1,2-diol. In an attempt to prepare quinaldoin from quinoline-2-aldehyde and potassium cyanide, Buehler and Harris [10] reported the formation of a compound they thought to be this diol, on the basis of its formula and formation of a dibenzoate. Their observations have been confirmed and their diol shown to be identical with ours. As further confirmation of its structure, we have oxidised the diol to quinoline-2-aldehyde using periodic acid though the yield was less than 2 mol. per mol. of diol. Heating the

[7] Thayer and Corson, *J. Amer. Chem. Soc.*, 1948, **70**, 2330.
[8] Battersby and Edwards, *Chem. Soc. Special Publn.* No. 3, 1955, p. 33.
[9] Kaplan and Lindwall, *J. Amer. Chem. Soc.*, 1943, **65**, 927.
[10] Buehler and Harris, *J. Amer. Chem. Soc.*, 1950, **72**, 5015.

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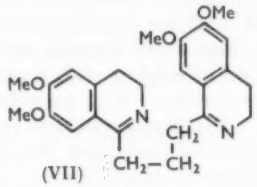
diol with small amounts of acetic or benzoic acid gave a mixture of 1,2-di-2′-quinolylethane and 1,2-di-2′-quinolylethanone. Attempted synthesis of the diol by addition of bromine to 1,2-di-2′-quinolylethylene and hydrolysis of the dibromide gave only 1,2-di-2′-quinolylacetylene.

The preparation of 1,2-di-2′-quinolylethylene has been described by several workers. Thayer and Corson [7] dehydrated 1,2-di-2′-quinolylethanol with acetic anhydride and



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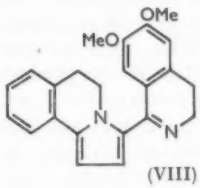

(VIII)

acetic acid and described the product as " yellow-orange " needles. We find that the *trans*-olefin is almost colourless, in agreement with Hammick *et al.*,[5] and that the orange impurity was 1,2-di-2′-quinolylethanone. Heating the diquinolylethanol with glacial acetic or benzoic acid affords a mixture of approximately equal amounts of the diquinolylethanone and diquinolylethane. The mechanism of this reaction is being further studied.

Experimental

Action of Sulphuric Acid on Quinaldine.—Quinaldine (28 g., 3 mol.) and concentrated sulphuric acid (6·6 g., 1 mol.) were refluxed together during 5 hr. The product, a dark red viscous liquid, was treated with an excess of 15% sodium hydroxide solution and steam-distilled to remove unchanged quinaldine (15·2 g.). The residue (9·3 g.) was dissolved in benzene (200 ml.) and extracted with 0·1N-hydrochloric acid (4 × 100 ml.), and the extracts were basified with sodium hydroxide solution. The oily base which was precipitated became granular when shaken. Trituration with cold acetone (10 ml.) and crystallisation of the residual solid from aqueous ethanol yielded 1,2-di-2′-quinolylethane (1·3 g.) as colourless needles, m. p. 163° (Found: C, 83·7; H, 5·7; N, 10·0. Calc. for $C_{20}H_{16}N_2$: C, 84·5; H, 5·7; N, 9·9%). Its picrate crystallised from ethanol as orange needles, m. p. 267° (decomp.). Concentration of the acetone solution yielded a dark brown viscous product (2·7 g.). The original benzene solution was washed with alkali, dried, and evaporated. Trituration of the residue with cold acetone (10 ml.) gave *1,2-di-2′-quinolylpyrrolo*[1,2-a]*quinoline* which crystallised from ethyl acetate–light petroleum as pale yellow needles (0·5 g.), m. p. 197° (Found: C, 85·1; H, 4·6; N, 10·0%; *M*, 440. $C_{30}H_{19}N_3$ requires C, 85·5; H, 4·5; N, 10·0%; *M*, 421). Its *picrate*, crystallised from ethanol, had m. p. 265° (Found: C, 66·2; H, 3·5; N, 12·5. $C_{36}H_{22}N_6O_7$ requires C, 66·5; H, 3·4; N, 12·9%). The *methiodide* crystallised as red needles (from ethanol), m. p. 219° (Found: I, 21·0. $C_{31}H_{22}IN_3$ requires I, 22·5%). Evaporation of the acetone solution yielded a dark brown viscous residue (2·6 g.).

Action of Sulphur on Quinaldine.—Quinaldine (29 g.) and sulphur (3·2 g.) were heated at the b. p. during 4 hr. Hydrogen sulphide was evolved. The dark brown solution was steam-distilled, and the residue dissolved in 5N-hydrochloric acid (100 ml.) and filtered. The filtrate was basified and the precipitated bases were extracted with benzene. Washing the benzene solution with 0·1N-hydrochloric acid (6 × 100 ml.) and basification of the extracts yielded initially an oil but finally a granular solid (3·1 g.). Crystallisation from ethyl acetate–light petroleum gave diquinolylethane, m. p. 164°, as needles. Evaporation of the benzene solution yielded a viscous oil which deposited a pale brown base (1·86 g.) on trituration with a little acetone. The base (I; R = 2-quinolyl), gave yellow needles, m. p. 197° (from ethyl acetate–light petroleum).

Oxidation of 1,2-Di-2′-quinolylpyrrolo[1,2-a]*quinoline.*—A solution of the base (0·5 g.) in pyridine (20 ml.) and water (20 ml.) was added to potassium permanganate (2 g.) in water (10 ml.), and the mixture refluxed during 2 hr. The precipitated manganese dioxide was filtered off and washed with hot water, and the filtrate and washings were made just acid with dilute sulphuric acid. Addition of an excess of concentrated copper sulphate solution afforded

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a precipitate (0·48 g.) which was suspended in boiling water (150 ml.). Hydrogen sulphide was passed into it for 1 hr. Removal of the precipitated copper sulphide and evaporation of the filtrate left a grey crystalline residue which deposited quinaldic acid (m. p. and mixed m. p. 153°) from light petroleum (b. p. 100—120°).

Hydrogenation of 1,2-*Di*-2′-*quinolylpyrrolo*[1,2-a]*quinoline*.—A solution of the base (0·078 g.) in ethanol (20 ml.) was shaken with hydrogen and Raney nickel (1 ml. settled suspension) in ethanol (40 ml.) for 2 hr. Filtration of the almost colourless solution (Filtercel) and removal of the ethanol under reduced pressure afforded a pale brown solid. Extraction of this with light petroleum removed material (0·069 g.) which, recrystallised from aqueous ethanol (charcoal), gave cream-coloured 1,2,3a,4,5-*hexahydro*-1,2-*di*-2′-*quinolylpyrrolo*[1,2-a]*quinoline*, m. p. 187° (Found: C, 84·2; H, 5·96; N, 9·8. $C_{30}H_{25}N_3$ requires C, 84·3; H, 5·90; N, 9·8%). The base gave a pale yellow hydrochloride.

1,2-*Di*-2′-*quinolylethylene*.—1,2-Di-2′-quinolylethane (0·57 g.) and selenium dioxide (0·44 g.) in dioxan (20 ml.) were refluxed together for 2 hr., then filtered, and cooled. The solid which was deposited (0·36 g.) crystallised from methanol to give 1,2-di-2′-quinolylethylene as pale yellow needles, m. p. 189° (Found: C, 84·9; H, 5·0; N, 9·9. Calc. for $C_{20}H_{14}N_2$: C, 85·1; H, 5·0; N, 9·9%). The *methiodide* crystallised from water as a pale yellow powder, m. p. 212—213°, which became orange on drying (Found: C, 58·6; H, 3·9; I, 31·0. $C_{21}H_{17}IN_2$ requires C, 59·4; H, 4·0; I, 30·0%).

1,2,3-*Tri*-2′-*quinolylpropane*.—Quinaldine (0·3 g., 3 mol.) 1,2-di-2′-quinolylethylene (0·2 g., 1 mol.), and quinaldine hydrochloride (0·13 g., 1 mol.) were heated together in a sealed tube at 100° during 3 hr. The product was extracted with benzene and water, and the benzene solution washed with dilute sodium hydroxide solution and concentrated. Extraction of the viscous residue with boiling light petroleum (b. p. 40—60°; 2 × 10 ml.) and concentration of the extract yielded pale yellow crystals (0·11 g.), m. p. 131—133°. Recrystallisation from light petroleum (b. p. 80—100°) gave 1,2,3-*tri*-2′-*quinolylpropane* as almost colourless needles, m. p. 136° (Found: C, 84·7; H, 5·5; N, 9·9. $C_{30}H_{27}N_3$ requires C, 84·7; H, 5·5; N, 9·9%). Alternatively, benzoic acid was used as catalyst at 165°.

Reaction between 1,2,3-*Tri*-2′-*quinolylpropane and Sulphur*.—The triquinolylpropane (0·5 g.) and sulphur (0·1 g.) were heated at 210° during 1 hr. After cooling, the product was triturated with 0·1N-hydrochloric acid (25 ml.) to remove unchanged triquinolylpropane, and the residue treated with 1·0N-hydrochloric acid (25 ml.). Basification of this red solution gave a cream-coloured solid (0·32 g.) which crystallised from ethyl acetate–light petroleum as yellow needles, m. p. 193°, shown to be the base (I; R = 2-quinolyl) by the m. p. and mixed m. p. of the methiodide.

Dehydrogenation of 2-*Phenyl*-1,3-*di*-2′-*quinolylpropane by Sulphur*.—2-Phenyl-1,3-di-2′-quinolylpropane (1·87 g.) and sulphur (0·32 g.) were heated together at 210° during 1 hr. The dark red product was dissolved in cold benzene (8 ml.) and chromatographed on alumina (Spence's type O). A brown residue remained at the top of the column and a wide orange band was eluted with benzene, yielding a viscous oil which on the addition of ethanol (3 ml.) deposited orange crystals (1·72 g.), m. p. 117—125°. Trituration of the crystals with cold acetone (2 × 3 ml.) yielded a brown solution containing a crystalline suspension. Separation of the suspension by centrifugation, and crystallisation from aqueous acetone, yielded pale yellow 2-*phenyl*-1-2′-*quinolylpyrrolo*[1,2-a]*quinoline* (0·82 g.), m. p. 154—155° (Found: C, 87·7; H, 4·7; N, 7·3. $C_{27}H_{18}N_2$ requires C, 87·6; H, 4·9; N, 7·6%). A further crop (0·13 g.), m. p. 150°, was obtained from the acetone mother-liquor.

Oxidation of 2-*Phenyl*-1,3-*di*-2′-*quinolylpropane with Mercuric Acetate*.—Hot solutions of 2-phenyl-1,3-di-2′-quinolylpropane (1·37 g.) in glacial acetic acid (4 ml.) and of mercuric acetate (3·2 g.) in acetic acid (4 ml.) and water (35 ml.) were mixed together and refluxed during 3 hr. The solution became yellow and mercurous acetate and an oil separated. After cooling, the solution was filtered, the residue was washed with warm acetone, and the washings were added to the filtrate. The filtrate was concentrated to remove the acetone, mercuric acetate (1·6 g.) added, and the solution refluxed for a further hour. On cooling and filtration of the solution, a small amount of mercurous acetate and mercury remained, together with organic material. This residue was extracted with hot acetone (3 × 25 ml.), and the solvent removed from the extract under reduced pressure. Trituration of the solid residue with 0·1N-hydrochloric acid removed any unchanged substituted propane. Extraction of the residue therefrom with a mixture of 1·0N-hydrochloric acid and methanol followed by basification of the deep red solution

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obtained yielded a yellow precipitate (0·46 g.) which crystallised from ethanol as yellow needles, m. p. 154°. The original aqueous filtrate containing the mercury salts was heated to the b. p. and hydrogen sulphide passed into it until the solution was cold. The precipitated mercuric sulphide was filtered off (Filtercel) and extracted with hot acetone (3 × 25 ml.). Concentration of the extract gave a green fluorescent solution which slowly deposited a small quantity of yellow needles, m. p. 153°.

The compound showed no depression of m. p. in admixture with the base obtained by dehydrogenation of 2-phenyl-1,3-di-2′-quinolylpropane with sulphur. The base gave a red *methiodide*, m. p. 228—229° (from ethanol–ether) (Found: C, 65·1; H, 4·2. $C_{29}H_{21}IN_2$ requires C, 65·6; H, 4·1%).

1,2-*Di*-2′-*quinolylethanol*.—Quinaldine (5 g.) and quinoline-2-aldehyde (5 g.) were refluxed in 1 : 4 v/v aqueous ethanol (25 ml.) during 30 hr., the solution being cooled at intervals of 6 hr. and the precipitates removed (7·2 g.). Extraction of the combined products with hot ethanol yielded a soluble product (6·0 g.) and an insoluble residue (1·2 g.). Crystallisation of the former from ethanol yielded 1,2-di-2′-quinolylethanol as plates (4·1 g.), m. p. 165°. The ethanol-insoluble material crystallised from dimethylformamide to give plates of 1,2-di-2′-quinolylethane-1,2-diol (1·0 g.), m. p. 210° (decomp.).

Oxidation of 1,2-*Di*-2′-*quinolylethane*-1,2-*diol*.—The diol (0·10 g.) and periodic acid (0·5 g.) in water (20 ml.) were kept at 80° during ½ hr. After cooling, the solution was basified and the white precipitate extracted with ether (3 × 20 ml.). The ethereal solution was dried and the solvent removed to leave a residue (0·09 g.), extraction of which with N-hydrochloric acid and addition of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid to the extract gave a yellow precipitate. After 2 hr. the precipitate was filtered off, washed, and dried (0·07 g.). Crystallisation from aqueous acetic acid gave yellow needles of quinoline-2-aldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 247—248°.

Attempted Hydrolysis of 1,2-*Dibromo*-1,2-*di*-2′-*quinolylethane*.—The bromo-compound (0·3 g.) was refluxed with potassium hydroxide (5·0 g.) in water (30 ml.) and dioxan (20 ml.) during 5 hr. When the solution was cooled a white base was precipitated which gave colourless crystals of 1,2-di-2′-quinolylacetylene, m. p. 182°, from dioxan. Under milder conditions there was no reaction.

Action of Benzoic Acid on 1,2-*Di*-2′-*quinolylethanol*.—The diquinolylethanol (0·31 g.) and benzoic acid (0·12 g.) were heated together in a sealed tube for 3 hr. at 100°. The product, which smelled of quinaldine, was dissolved in warm N-hydrochloric acid and the solution poured into an excess of cold dilute sodium hydroxide solution. The yellow precipitate (0·27 g.) was removed, treated with 0·05N-hydrochloric acid (3 × 15 ml.), and then basified to give a pale yellow precipitate (0·13 g.) which crystallised from light petroleum (b. p. 100—120°) as colourless needles of 1,2-di-2′-quinolylethane, m. p. and mixed m. p. 158° [picrate, m. p. 267° (decomp.)]. Treatment of the residue with hot N-hydrochloric acid and basification of the deep red solution gave an orange precipitate (0·14 g.) which crystallised from light petroleum (b. p. 100—120°) to give orange needles of 1,2-di-2′-quinolylethanone, m. p. 212° (Found: C, 80·1; H, 4·7; N, 9·4. Calc. for $C_{20}H_{14}N_2O$: C, 80·5; H, 4·7; N, 9·4%).

Action of Acetic Acid on 1,2-*Di*-2′-*quinolylethane*-1,2-*diol*.—The diol (0·54 g.) and glacial acetic acid (5 ml.) were refluxed together during 15 min., and the deep red solution cooled and poured into an excess of ice-cold dilute sodium hydroxide solution with stirring. The brown precipitate (0·41 g.) was extracted with 0·05N-hydrochloric acid (5 × 10 ml.) and the extracts were basified separately. The first two extracts yielded a cream-coloured base (0·07 g.) which crystallised from aqueous ethanol as pale yellow needles, m. p. 165°. Its picrate had m. p. 270° (decomp.) and a mixed m. p. of the base and 1,2-di-2′-quinolylethane showed no depression. Further treatment of the original brown base with hot N-hydrochloric acid and filtration and cooling of the filtrate yielded a sparingly soluble dark red hydrochloride; this afforded 1,2-di-2′-quinolylethanone (0·27 g.), m. p. and mixed m. p. 212°.

The authors are indebted to Mr. H. Higson for technical assistance during the early stages of this work.

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[*Received, July 6th*, 1960.]

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222. *The Reactions of Boron Chlorides with Acetone.*

By A. G. Massey.

Acetone and boron trichloride react rapidly at −78° to form a white solid of variable composition, which decomposes above −15° with evolution of hydrogen chloride. All three chlorine atoms of the boron trichloride can be lost as hydrogen chloride. Acetone and diboron tetrachloride react in a molar ratio of 2 : 1 or *ca.* 1 : 1 at −78° according to the conditions. Two moles of hydrogen chloride are evolved per mole of diboron tetrachloride when the mixture is heated to 100°; 2-chloropropane and t-butyl chloride are also formed. At 150° the amount of hydrogen chloride evolved decreases.

Greenwood and Perkins,[1] when attempting to measure the heat of solution of boron trichloride in acetone, noted that the expected 1 : 1 addition compound could not be isolated owing to its rapid decomposition to hydrogen chloride and resin. This reaction has now been studied more closely. Reaction was rapid at temperatures between −78° and −35° to form white solids which always contained acetone in excess of the amount required for 1 : 1 addition even when boron trichloride was used in excess. Increasing the temperature of reaction to 0° decreased the quantity of acetone associated with each mole of boron trichloride but side-reactions involving the elimination of hydrogen chloride then proceeded to a considerable extent, making it impossible to obtain the 1 : 1 addition compound pure. When the solid product was warmed to room temperature (22°) it rapidly melted to deep red liquid which evolved hydrogen chloride vigorously; the liquid, at room temperature or when heated, gradually solidified to a dark red polymer.

Three generalisations can be made about the thermal decomposition of the solid: (i) All three chlorine atoms of the original boron trichloride could be recovered as hydrogen chloride, provided sufficient acetone was present. (ii) More than two moles of hydrogen chloride were evolved per original mole of acetone at 135°. (iii) No alkyl chlorides were detected in any of the experiments.

Reaction of Acetone with Diboron Tetrachloride.—With excess of acetone, diboron tetrachloride formed a white adduct $2COMe_2,B_2Cl_4$ between −78° and −23° which slowly lost acetone on increase of temperature to 0°, the loss being accompanied by the formation of small quantities of hydrogen chloride. With diboron tetrachloride in excess, ratios approaching 1 : 1 could be achieved at −45°. The adducts so formed only slowly evolved hydrogen chloride at room temperature, forming red solids. On decomposition of the 2 : 1 adduct at temperatures up to 100°, two moles of hydrogen chloride were evolved per mole of diboron tetrachloride used. Ratios based on hydrogen chloride formed in reactions involving the boron chlorides are necessarily somewhat approximate owing to side reactions with water outgassed from the reaction vessel walls during the experiment; in this case, the maximum deviation was *ca.* 5%.

In contrast to the boron trichloride experiments, several alkyl chlorides were isolated among the decomposition products, those in the greatest yield being 2-chloropropane and t-butyl chloride. Increasing the decomposition temperature to 150° caused the ratio $HCl : B_2Cl_4$ to fall well below the 2 : 1 value noted above, indicating a secondary reaction between the polymeric residue and the hydrogen chloride initially evolved. Methylboron dichloride, $CH_3{\cdot}BCl_2$, could also be isolated in small yield during the decomposition of adducts containing a deficiency of acetone from the 2 : 1 ratio. This probably indicated the presence of boron–carbon bonds in the residues, since it is known that compounds such as B_2X_4,C_2H_4 (X = halogen) evolve alkylboron dihalides on pyrolysis.[2,3]

[1] Greenwood and Perkins, *J.*, 1960, 356.
[2] Holliday and Massey, *J.*, 1960, 2075.
[3] Ceron, Finch, Frey, Kerrigan, Parsons, Urry, and Schlesinger, *J. Amer. Chem. Soc.*, 1959, **81**, 6388.

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Experimental

The materials were handled in a conventional high-vacuum apparatus equipped with mercury-float valves. Acetone was purified *via* its sodium iodide complex,[4] which was allowed to dissociate under vacuum: v. p. 67 mm. at 0°, 175 mm. at 20°. The preparation of diboron tetrachloride has been described previously.[5] Boron trichloride was fractionated through baths held at −78° and −112°; v. p. 476 mm. at 0°. Unless otherwise stated all the quantities recorded below are in terms of mmoles or mequivs.

Reaction of Boron Trichloride with Acetone.—Acetone and boron trichloride (excess) were condensed into a reaction vessel at −196°, and the mixture was warmed to −78° (or −35°); a rapid reaction ensued, forming a white solid. The excess of boron trichloride was then removed, purified from traces of hydrogen chloride by fractionation at −126°, and measured. In a typical experiment boron trichloride (1·73) and acetone (1·06) were allowed to react for 2 hr. at −78°; 1·19 mmoles of boron trichloride and 0·06 mmole of hydrogen chloride were the sole volatile products. Hence $COMe_2 : BCl_3 = 1·96 : 1$. On warming the white solids formed at −78° or −35°, rapid coloration started at −6°, −8° to −9°, and −9° in three independent experiments, the coloration being accompanied by evolution of hydrogen chloride. Very slow coloration was also noted in a sample of solid held at −15° for long periods. The decomposition of the solid at higher temperatures was studied by allowing the acetone and boron trichloride to react as above at −78°, the reaction tube was then sealed and held at the required temperature for some arbitrary time. When the tube, cooled to −196°, was opened to the vacuum apparatus, any non-condensable gases present were removed by the Töpler pump and identified by combustion analysis. The material volatile at −126° was shown to be hydrogen chloride by vapour-density and vapour-pressure determinations. The remaining volatile material was identified by its infrared spectrum, any boron trichloride present being estimated by hydrolysing a sample with distilled water and titrating the resulting hydrochloric and boric acids. Two experiments are summarised below: (1) Acetone (1·80) and boron trichloride (0·84) after reaction at −78° were held at 23° for 14 hr.; hydrogen chloride (1·75) and boron trichloride (0·03) were the only volatile products. Heating for 4 hr. at 90° produced hydrogen chloride (0·49) and boron trichloride (0·07). Hence, total hydrogen chloride produced = 2·24, boron trichloride used = 0·74. Thus the ratio $HCl : BCl_3 = 3·03 : 1$. (ii) Acetone (0·85) and boron trichloride (1·65) were heated at 100° for 7 hr. Hydrogen chloride (1·63) and boron trichloride (0·87) were recovered. Acetone : $HCl = 1 : 1·91$. Heating the mixture at 135° for a further 12 hr. produced more hydrogen chloride (0·15) and boron trichloride (0·05). Ratio, acetone : $HCl = 1 : 2·11$. The boron and chlorine remaining in the residues were readily titratable after hydrolysis with distilled water at room temperature.

Reaction of Acetone with Diboron Tetrachloride.—The experiments were conducted similarly to those with boron trichloride and acetone. Acetone (3·13) and diboron tetrachloride (0·86) were allowed to react at −78° for one hr., 1·36 mmoles of acetone then being recovered; ratio $COMe_2 : B_2Cl_4 = 2·06 : 1$. In an experiment employing an excess of diboron tetrachloride (0·83) over acetone (0·72), 0·22 mmole of diboron tetrachloride was removed after 10 min. at −45°; ratio, $COMe_2 : B_2Cl_4 = 1·18 : 1$.

The decomposition of the 2 : 1 adduct was studied by allowing measured quantities of diboron tetrachloride and acetone to react at −78°, the white adduct being rapidly formed. The reaction tube was then sealed and held at the required temperature as in the boron trichloride experiments. The hydrogen chloride isolated from these experiments contained *ca.* 2% of an impurity which, from its volatility at −126° and the fact that it absorbed in the C–H region of the infrared spectrum, was assumed to be a lower alkane but was not positively identified. Owing to its presence, the quantity of hydrogen chloride in the −126° volatile material had to be estimated by titration. In the experiments with boron trichloride the same impurity was present but in amounts much less than the experimental error involved in the measurement of the vapour density or volume of the hydrogen chloride; hence its presence could be neglected. A summary of several experiments conducted under various conditions of temperature, time, and concentration of reactants is shown in the Table; methylboron dichloride was isolated in those experiments marked by an asterisk. Fraction X

[4] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., 1954, p. 170.
[5] Holliday and Massey, *J.*, 1960, 43.

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contained several alkyl chlorides, mainly 2-chloropropane and t-butyl chloride; in experiments 3 and 7 the fraction also contained small quantities of excess of acetone.

Decomposition of the acetone–diboron tetrachloride adduct.

Expt. No.	1*	2*	3	4*	5	6	7	8*	9
B_2Cl_4 added	0·86	0·46	0·82	1·00	0·83	0·89	0·65	0·91	0·93
Acetone added	1·77	0·72	3·37	1·77	1·84	1·76	3·02	1·44	0·96
Reaction time, hr.	2	1	3	3	10	10	6	16	19
Reaction temp.	90°	100°	100°	100°	100°	100°	150°	150°	150°
Reaction products: H_2	—	—	0·03	—	—	trace	0·20	—	—
CH_4	1·80	0·76	1·72	2·08	1·73	1·82	1·04	1·60	1·22
BCl_3	0·20	0·35	0·00	0·11	0·12	0·18	0·00	0·35	0·58
X			0·50	0·09	0·17	0·12	1·13	0·18	0·44
Residues: Hydrolysis H_2	—	—	0·34	—	0·07	0·05	0·26	—	—
Cl^-	—	0·30	0·88	1·05	0·90	0·85	0·35	0·36	0·35
B	—	—	—	1·36	1·70	1·54	—	1·10	0·72
Ratio B_2Cl_4 : HCl	1 : 2·09	1 : 1·65	1 : 2·10	1 : 2·08	1 : 2·08	1 : 2·05	1 : 1·60	1 : 1·76	1 : 1·31

The author thanks Dr. A. K. Holliday for his continued interest in this work, and the Department of Scientific and Industrial Research for a maintenance grant.

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223. *Studies in the Preparation of* B-*Nor-diterpenoids.*

By John Frederick Grove and B. J. Riley.

The 11-hydroxy-9,10-diketones obtained by oxidation of methyl abieta-5,7,13(14)-trien-15-oate and the enantiomer of methyl 10-hydroxy-9-oxopodocarpa-5,7,10,13(14)-tetraen-16-oate with chromic oxide are shown by infrared studies to have the 11α- and 11β-configuration respectively. A mechanism for the formation of the hydroxy-diketones is discussed. Benzilic acid rearrangement of the enantiomer of methyl 9,10-dioxo-11β-podocarpa-5,7,13(14)-trien-16-oate gave 1,2,3,4,10α,11-hexahydro-9β-hydroxy-1β,11α-dimethylfluorene-1α,9α-dicarboxylic acid, the stereochemistry of which was deduced from the reactions of its anhydride. Under similar conditions methyl 11-hydroxy-9,10-dioxopodocarpa-5,7,13(14)-trien-15-oate gave (−)-1,2,3,6,7,11b-hexahydro-4,11b-dimethyl-6,7-dioxodibenz[*b*,*d*]oxepin.

Gibberellic acid (I),[1] the plant-growth promoting substance obtained[2] from *Gibberella fujikuroi*, has been shown[3] to be a diterpenoid in which, in addition to other structural modifications, contraction of ring B of the pimarane skeleton (II) to the perhydrofluorene skeleton (III) has occurred with extrusion of one carbon atom as a carboxyl group.

This paper records attempts to contract ring B of some resin acid analogues * to compounds with a hydrofluorene skeleton. These attempts were only successful with the enantiomer[4,5] (IV; R = H, absolute configuration) of 11β-podocarpa-5,7,13(14)-trien-16-oic acid † in which rings A/B are *cis*-fused, inversion at position 12 in podocarpa-5,7,13(14)-trien-15-oic acid (deisopropyldehydroabietic acid) having been effected with

* The absolute configuration of gibberellic acid was unknown when this work was commenced.

† The nomenclature used is that of Klyne, *J.*, 1953, 3072. The names deisopropylallodehydroabietic acid [5] and 5-isodeoxypodocarpic acid enantiomer [6] have also been used for (IV; R = H).

[1] Cross, Grove, McCloskey, Mulholland, and Klyne, *Chem. and Ind.*, 1959, 1345; Edwards, Nicolson Apsimon, and Whalley, *Chem. and Ind.*, 1960, 624.
[2] Cross, *J.*, 1954, 4670.
[3] Birch, Rickards, and Smith, *Proc. Chem. Soc.*, 1958, 192.
[4] Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 2631.
[5] Ohta and Ohmori, *Pharm. Bull.* (*Japan*), 1957, **5**, 91, 96.
[6] Wenkert and Chamberlin, *J. Amer. Chem. Soc.*, 1959, **81**, 688.

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aluminium chloride in benzene. Only with *cis*-fusion of rings A/B was a 9,10-diketone obtained which could be subjected to ring contraction.

Oxidation of the ester (IV; R = Me) by chromic oxide gave the 9,10-diketo-ester [5] (V) which formed a quinoxaline derivative (cf. Ohta [7]) and, on benzilic acid rearrangement, smoothly gave the acid (VI; R = H). The best yields of the acid (VI; R = H) were obtained with boiling 10% sodium hydroxide.

Wenkert and his co-workers [6,8] found that chromic oxide oxidised the A/B-*trans*-compounds, methyl abieta-5,7,13(14)-trien-15-oate (methyl dehydroabietate) and the nitrile of podocarpa-5,7,13(14)-trien-15-oic acid, to the corresponding 9-ketones only. By more vigorous oxidation Ohta and Ohmori [5] converted methyl podocarpa-5,7,13(14)-trien-15-oate into a hydroxy-9,10-diketone which they assumed to be the 11-hydroxy-compound. In the present study the formation of an 11-hydroxy-compound from methyl podocarpa-5,7,13(14)-trien-15-oate has been confirmed, and, in addition, the 11-hydroxy-9,10-dioxo-derivative (VII; R = Pr^i, R′ = CO_2Me) has been obtained from methyl abieta-5,7,13(14)-trien-15-oate. The 11-hydroxy-9,10-diketones are equivalent to *o*-(2-oxocyclohexyl)phenylglyoxals (open form) and under the conditions of the benzilic acid rearrangement do not undergo contraction of ring B; even in an atmosphere of nitrogen (although oxygen was not rigorously excluded from the reactants) the hydroxy-diketone (VII; R = H, R′ = CO_2Me) gave the oxepin derivative (VIII) and carbon dioxide, the latter being eliminated from the intermediate open-chain β-keto-ester (IX). The formation of compound (IX) from the monohydrate of the dione (VII; R = H, R′ = CO_2Me) may be regarded as a retroaldol reaction or, more generally, as a case of ring-chain tautomerism. The formation of the oxepin derivative (VIII), which liberated carbon monoxide on treatment with phosphoric acid, and the oxidation of the hydroxy-diketone (VII; R = H, R′ = CO_2Me) under more vigorous conditions to the acid (X; R = H; lactol form) confirm the structure of the hydroxy-diketone.

The α-oxidation of a methylene-ketone by chromic oxide may be considered (cf. refs. 6 and 8) to take place by a mechanism whereby disproportionation of the initially formed enol chromate to the α-ketol chromite is followed by liberation of the α-ketol. If it is assumed, similarly, that the oxidation of αβ-diketones to γ-hydroxy-αβ-diketones is dependent upon enolisation of the β-keto-group as the initial step, then the difference towards chromic oxide oxidation of diterpenoids with rings A/B *cis*- and *trans*-fused can be explained. Molecular models show there is no restriction on the enolisation of methyl 9,10-dioxopodocarpa-5,7,13(14)-trien-15-oate; but enolisation of the diketo-ester (V), in which the 12-methyl group is equatorial, brings about a conformational change in ring A and leads to 1,3-diaxial interaction between the 1-methoxycarbonyl and the 12-methyl group. This barrier to enolisation allows the isolation of the diketo-ester (V) as a stable oxidation product: however, once formed, the enol (XI; R = Me, R′ = H) is stabilized by hydrogen bonding with the 9-keto-group.

Like the enantiomer of the nitrile [8] of 9,10-dioxo-11β-podocarpa-5,7,13(14)-trien-16-oic acid the ester (V) gave no colour with ferric chloride. Hydrolysis of the ester (V) occurred with 5% aqueous ethanolic potassium hydroxide, and gave the enol (XI; R = R′ = H), which gave a red colour with ferric chloride. In alkaline solution, the ultraviolet spectra of this enol and the diketone (V) were identical. The infrared spectrum of the enol showed a band at 1634 $cm.^{-1}$ consistent with the presence of a conjugated ketone bonded to the adjacent hydroxyl group. This band appeared again at 1633 $cm.^{-1}$ in the methyl ester (XI; R = Me, R′ = H) but shifted to the normal conjugated-ketone position at 1655 $cm.^{-1}$ in the methyl ether (XI; R = R′ = Me). Some ketonisation of the enol ester (XI; R = Me, R′ = H) took place in carbon tetrachloride, as shown by the appearance of bands near 1725 and 1700 $cm.^{-1}$ in addition to the 1733 $cm.^{-1}$ (ester) and the 1633 $cm.^{-1}$ band.

[7] Ohta, *Pharm. Bull.* (*Japan*), 1957, **5**, 256.
[8] Wenkert and Jackson, *J. Amer. Chem. Soc.*, 1958, **80**, 211.

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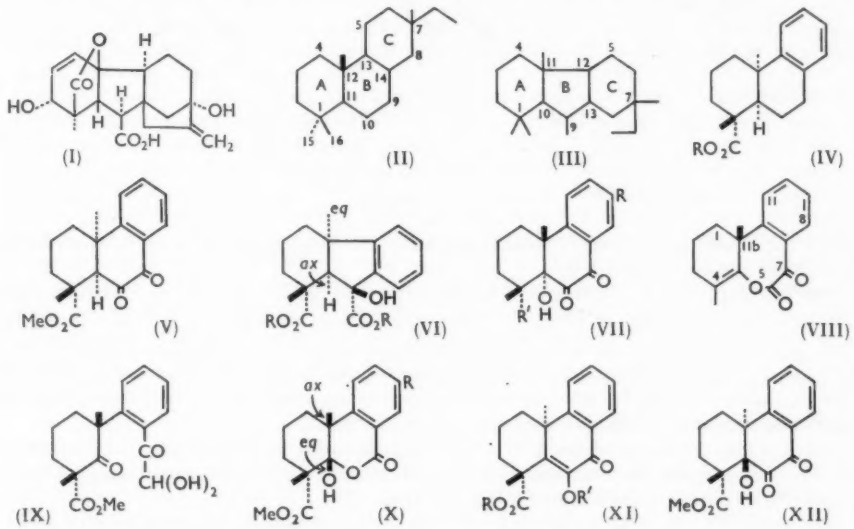
Oxidation of the enol-ester (XI; R = Me, R′ = H) by chromic oxide gave the enantiomer (XII) of methyl 11-hydroxy-9,10-dioxopodocarpa-5,7,13(14)-trien-16-oate. Oxidation presumably occurred at the β-face since both the 1-methoxycarbonyl and the 12-methyl group are α-axial, and the possibility of subsequent rearrangement to the A/B-*cis*-11α-hydroxy-compound is excluded by the infrared spectrum in solution [$\nu_{max.}$ 3600, 1736 (broad and intense) and 1695 cm.$^{-1}$] which showed no hydrogen bonding between the



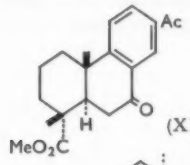
11-hydroxy-substituent and the 10-keto- or 1-methoxycarbonyl group. As expected for a compound with the 11α-configuration, the 11-hydroxy-diketone [9] (VII; R = H, R′ = Me), $\nu_{max.}$ 1731 and 1690 cm.$^{-1}$, also showed no intramolecular hydrogen bonding. Such bonding occurred in both the esters (VII; R = H and Pr^{i}, R′ = CO_2Me), $\nu_{max.}$ near 3300, 1736, 1695 cm.$^{-1}$ (broad and intense), and in the quinoxaline derivative of (VII; R = H, R′ = CO_2Me), $\nu_{max.}$ 1685 cm.$^{-1}$, between the 11-hydroxy- and the 1-methoxycarbonyl substituent, consistent with the 11α-configuration expected from attack at the less obstructed α-face. Further oxidation of the ester (VII; R = H, R′ = CO_2Me) with chromic oxide gave the acidic methyl 3-*o*-carboxyphenyl-1,3-dimethyl-2-oxocyclohexanecarboxylate [5,7] (lactol form; X; R = H) which was also obtained directly from methyl podocarpa-5,7,13(14)-trien-15-oate.

In addition to the ester (VII; R = Pr^{i}, R′ = CO_2Me) and the ketone [10] (XIII) which were isolated from the neutral fraction, oxidation of methyl abieta-5,7,13(14)-trien-15-oate by chromic oxide gave an acidic product (X; R = Ac). Both acids (X; R = H and Ac) were insoluble in sodium hydrogen carbonate, and the infrared spectra were consistent only with their formulation as lactols,[5] the more probable configuration of the 11-hydroxy-substituent being β(equatorial). There was no intramolecular hydrogen bonding with the 1-methoxycarbonyl group.

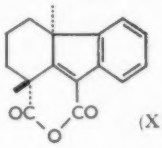
With acetic anhydride the acid (VI; R = H) gave a mixture of anhydrides (XIV) and (XV), which on alkaline hydrolysis gave the same product (XVI; R = R′ = H). Two centres, at positions 9 and 10, have been involved in the formation of the acid (VI; R = H), but of the four possible stereoisomeric structures for this acid, molecular models

[9] Hodges and Raphael, *J.*, 1960, 50.
[10] Ritchie, Sanderson, and McBurney, *J. Amer. Chem. Soc.*, 1954, **76**, 723; Zeiss and Tsutsui, *ibid.*, 1955, **77**, 6706.

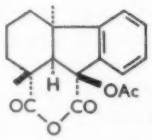
show that only three are capable of anhydride formation and of these only one, namely (VI; R = H), gives an acetoxy-anhydride in which the 10-hydrogen atom and the 9-acetoxy-group are *trans* and near-coplanar and therefore capable of ready elimination. Moreover, in form (VI; R = H) the 1-carboxylic acid and the 11-methyl group are



(XIII)

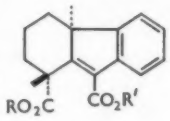


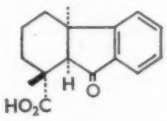
(XIV)



(XV)

(XVI)





(XVII)

equatorial; there is a strong 1,3-diaxial interaction between these groups in structures where rings A/B are *trans*-fused.

The introduction of a 9,10-double bond in the acid (XVI; R = R′ = H) brings about a conformational change in ring A. The axial configuration of the 1-methoxycarbonyl group in the ester (XVI; R = R′ = Me) was confirmed by the formation of the half-ester (XVI; R = Me, R′ = H) under conditions which hydrolyse the equatorial ester substituent in methyl abieta-5,7,13(14)-trien-15-oate but leave the axial ester substituent of methyl 6-hydroxypodocarpa-5,7,13(14)-trien-16-oate unaffected.[11]

Lead tetra-acetate oxidises the acid (VI; R = H) to the hexahydrofluorenone[7] (XVII). Here again, as with the acid (VI; R = H), the more stable configuration at position 10 is that in which rings A/B are *cis*-fused.

The acids (VI; R = H) and (XVI; R = R′ = H) showed no plant-growth promoting properties when applied to the leaves of intact dwarf-pea seedlings.[12] The lactols (X; R = H and were likewise inactive.

Experimental

M. p.s (Kofler block) were corrected. Unless otherwise stated, ultraviolet absorption spectra and optical rotations were determined for EtOH solutions, and infrared spectra were obtained for Nujol "mulls." Light petroleum had b. p. 60—80°. Silica of 100—200 mesh size was used in chromatography.

Methyl 9,10-dioxo-11β-podocarpa-5,7,13(14)-trien-16-oate enantiomer (V), m. p. 137—138°, $[\alpha]_D^{23}$ −218° (*c* 0·4), was prepared by oxidation of methyl 11β-podocarpa-5,7,13(14)-trien-16-oate enantiomer[5] (IV; R = Me) with chromic oxide. The infrared spectrum of a dilute solution in carbon tetrachloride showed C=O bands at 1729 (ester and 10-ketone) and 1686 $cm.^{-1}$ (9-ketone).

The *quinoxaline derivative* formed a glass [after short-path distillation at 110—115° (bath)/8·3 × 10^{-5} mm.], m. p. 61—69° (Found: C, 77·3; H, 6·7; N, 7·6. $C_{24}H_{24}N_2O_2$ requires C, 77·4; H, 6·5; N, 7·5%). It gave an orange-red colour with concentrated sulphuric acid.

Action of Alkali on the Diketo-ester (V).—(A) *2·5N-Sodium hydroxide.* The ester (V) (1 g.) in 2·5N-sodium hydroxide (200 ml.) was heated under reflux for 3 hr. The cooled solution was acidified with concentrated hydrochloric acid (46 ml.) and extracted with ether. The ethereal extract was separated into acid and neutral fractions. Crystallisation of the acid fraction from methanol and then acetone gave *1,2,3,4,10α,11-hexahydro-9β-hydroxy-1β,11α-dimethylfluorene-1α,9α-dicarboxylic acid* (VI; R = H) (738 mg., 74%) as prismatic needles, m. p. 179—180° (decomp.), $[\alpha]_D^{25}$ −30·6° (*c* 1·0) [Found, dried at 100°: C, 66·3; H, 7·2. $C_{17}H_{20}O_5,(CH_3)_2CO$ requires C, 66·3; H, 7·2%. Found, dried at 140°: C, 66·9; H, 6·6%; equiv., 154. $C_{17}H_{20}O_5$

[11] Sherwood and Short, *J.*, 1938, 1006.
[12] Moffatt and Radley, *J. Sci. Food Agric.*, 1960, 386.

requires C, 67·1; H, 6·6%; equiv. (dibasic), 152], $\lambda_{max.}$ 264, ~270—272 mμ (log ε 3·1, 3·0 respectively), $\nu_{max.}$ 3400 (broad, bonded OH), 3175—2630 (broad, OH of CO_2H), 1706 (CO of CO_2H), 1607 (aromatic ring), or (in CCl_4) 3535 (OH), 1700 cm.$^{-1}$ (CO of CO_2H).

Crystallisation from methanol gave the *methanol solvate* as prisms, m. p. 172—173° (loss of solvent) (Found, dried at 100°: C, 64·8; H, 7·3%; equiv., 163. $C_{17}H_{20}O_5,CH_3OH$ requires C, 64·3; H, 7·2%; equiv., 168).

The *methyl ester* (VI; R = Me), prepared with ethereal diazomethane, crystallised from ether in prismatic needles, m. p. 98—100° (Found: C, 69·1; H, 7·4; OMe, 17·4. $C_{19}H_{24}O_5$ requires C, 68·7; H, 7·3; 2OMe, 18·7%), $\nu_{max.}$ 3595 (OH), 1724 (ester CO), 1600 cm.$^{-1}$ (aromatic ring).

When the reaction was carried out with 30% sodium hydroxide for 20 hr. the yield of the acid (VI; R = H) fell to 53%.

(B) 5% *Aqueous-ethanolic potassium hydroxide.* The ester (V) (24 mg.) was heated under reflux for 2 hr. with potassium hydroxide (190 mg.) in ethanol (2 ml.) and water (2 ml.). An orange colour developed which reverted to yellow on cooling. The solution was acidified, and extracted with ether. The ether extract was washed with 2N-sodium carbonate and evaporated, giving a yellow intractable gum (1·5 mg.). Acidification of the sodium carbonate solution and extraction with ether gave, on recovery, a gum (19 mg.) which slowly crystallised from benzene–light petroleum in prisms (6 mg.), m. p. 94—105°, of *10-hydroxy-9-oxopodocarpa-5,7,10,13(14)-tetraen-16-oic acid enantiomer* (XI; R = R′ = H), $\nu_{max.}$ 3200 (broad, OH), 2650 (OH of CO_2H); 1705 (carboxylic acid CO), 1634 (bonded, conjugated CO), 1599 cm.$^{-1}$ (aromatic ring), $\lambda_{max.}$ 260, 304 mμ (log ε 3·86, 3·87 respectively) changed to $\lambda_{max.}$ 241, 302 mμ (log ε 3·96, 3·53 respectively) on addition of 1 drop of 3N-sodium hydroxide. The same spectrum was obtained on addition of 3N-sodium hydroxide to the diketo-ester (V). Unlike the diketo-ester (V), the enol (XI; R = R′ = H) gave a red colour with ferric chloride and decolorized potassium permanganate in acetone.

The *methyl ester* (XI; R = Me, R′ = H), prepared with ethereal diazomethane, was an oil, b. p. 90° (bath)/2·3 × 10^{-4} mm. (Found: C, 71·7; H, 6·8. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7%), $\nu_{max.}$ (film) 3380 (OH), 1730 (ester CO), 1635 (bonded conjugated CO), 1602, 1572 cm.$^{-1}$ (aromatic ring), $\nu_{max.}$ (in CCl_4, dilute solution) 3514 (weak, broad) 3392, 3339 (bonded OH), 1733 (ester CO), 1633 cm.$^{-1}$ (bonded conjugated CO), together with 1724, 1703 cm.$^{-1}$ (9,10-diketone CO), contributed by form (V).

Treatment of the ester (XI; R = Me, R′ = H) in methanol with ethereal diazomethane for 24 hr. gave, after recovery and short-path distillation at 110—120° (bath)/1·3 × 10^{-4} mm., the *methyl ether* (XI; R = R′ = Me) as an oil (Found: C, 72·6; H, 7·2; OMe, 18·7. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·1; 2OMe, 19·7%), $\nu_{max.}$ (film) 1738 (ester CO), 1655 (conjugated CO), 1619 (enol ether), 1603, 1577 cm.$^{-1}$ (aromatic ring), $\lambda_{max.}$ 260, 290 mμ (log ε 3·99, 3·98 respectively).

Only intractable products were obtained when the ester (V) was heated under reflux with 20% butanolic potassium hydroxide (1·5 hr.) or with sodium methoxide in methanol (3 hr.).

Oxidation of the Enol Ester (XI; R = Me; R′ = H).—The enol-ester (XI; R = Me, R′ = H) (25 mg.), in acetic acid (1 ml.) was treated dropwise with chromium trioxide (9 mg.) in acetic acid (1 ml.) and water (0·25 ml.). The mixture was heated at 60° for 2 hr. and kept at room temperature for 18 hr. When worked up as described below for methyl podocarpa-5,6,13(14)-trien-15-oate, gummy acidic (5 mg.) and yellow neutral (20 mg.) fractions were obtained. Chromatography of the neutral fraction on silica gel (1 g.), and elution with benzene–ether (19 : 1) gave a homogeneous product which crystallised from benzene–light petroleum in yellow needles of *methyl 11-hydroxy-9,10-dioxopodocarpa-5,7,13(14)-trien-16-oate enantiomer* (XII), m. p. 164—167° (15 mg.) (Found: C, 68·1; H, 6·3. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·4%), $\nu_{max.}$ 3425 (OH), 1736, 1695 (ester and 9,10-diketone C=O), 1595 cm.$^{-1}$ (aromatic ring), or (in $CHCl_3$) 3600 (OH), 1732 (ester and 10-ketone CO), 1699 (9-ketone C=O), 1599 cm.$^{-1}$ aromatic ring).

Anhydrides from the Acid (VI; R = H).—The acid (VI; R = H) (300 mg.) in acetic anhydride (6 ml.) was heated under reflux for 1½ hr. After removal of the solvent *in vacuo*, the residue was fractionally crystallised from acetone, giving (i) *2,3,4,11-tetrahydro-1β,11α-dimethyl-1H-fluorene-1α,9-dicarboxylic anhydride* (XIV) (87 mg., 33%), needles (changing to rectangular plates above 170°), m. p. 208—209° (decomp.) (Found: C, 76·0; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%), $\lambda_{max.}$ 240, ~270—272 mμ (log ε 3·85, 3·1 respectively), $\nu_{max.}$ 1786, 1763 (C=O of αβ-unsaturated 6-ring anhydride), 1640 (conjugated C=C), and 1607 cm.$^{-1}$ (aromatic ring); and (ii) *9β-acetoxy-1,2,3,4,10α,11-hexahydro-1β,11α-dimethylfluorene-1α,9α-dicarboxylic*

anhydride (XV), prisms (64 mg., 19%), m. p. 163—165° (Found: C, 69·3; H, 6·1. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%), $\nu_{max.}$ 1816, 1764 (C=O of 6-ring anhydride), 1742, 1230 (OAc), 1615 cm.$^{-1}$ (aromatic ring). When the reaction time was extended to 2 hr., the anhydride (XIV) was isolated in 53% yield, but none of the acetoxy-anhydride (XV) was found.

Alkaline Hydrolysis of the Anhydride (XIV).—The anhydride (6 mg.) in N-sodium hydroxide (2 ml.) was shaken at room temperature for 20 hr. Acidification gave a precipitate which was filtered off and crystallised from dilute methanol, giving 2,3,4,11-*tetrahydro*-1β,11α-*dimethyl*-1H-*fluorene*-1α,9-*dicarboxylic acid* (XVI; R = R′ = H), needles (5 mg.), m. p. 210—212° (Found: C, 71·2; H, 6·3%; equiv., 128. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%; equiv., 143), $\lambda_{max.}$ 266 mμ (log ε 3·86), $\nu_{max.}$ 3285, 2655 (broad; OH of CO_2H), 1739, 1691 (CO of CO_2H), 1600 (conjugated C=C), 1590, 1574 cm.$^{-1}$ (aromatic ring). The acid was stable to 3N-sulphuric acid under reflux and to concentrated sulphuric acid at −10°.

The *methyl ester* (XVI; R = R′ = Me), prepared with diazomethane, formed needles, m. p. 118—119° (Found: C, 72·3; H, 6·9. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·1%).

Hydrolysis of the Ester (XVI; R = R′ = Me).—The ester (15 mg.) in 0·5N-ethanolic potassium hydroxide was heated under reflux for 2 hr. After dilution with water, the solution was extracted with ether, and the extract was separated into acidic (9 mg.) and neutral (6 mg.) fractions. The acid fraction was chromatographed on silica gel (1 g.) in ether and gave the homogeneous half-ester (XVI; R = Me, R′ = H) which crystallised from ether in needles (8 mg.), m. p. 135—139°, $\nu_{max.}$ 3460—2500 (broad, weak; OH of CO_2H), 1730 (ester CO), 1699 sh, 1684 (CO of CO_2H), 1598, 1575 cm.$^{-1}$ (aromatic ring).

Hydrolysis of Methyl Abieta-5,7,13(14)-*trien*-15-*oate*.—The ester (50 mg.) in 0·5N-ethanolic potassium hydroxide (20 ml.) was heated under reflux for 2 hr. After dilution with water the solution was extracted with ether and the extract was separated into acidic (10 mg.) and neutral (39 mg.) fractions. The acid fraction crystallised from hexane and was identified (infrared spectrum) as abieta-5,7,13(14)-trien-15-oic acid.

Alkaline Hydrolysis of the Anhydride (XV).—The anhydride (10 mg.), in 2N-sodium hydroxide (5 ml.), was heated under reflux for 2 hr. Acidification and recovery in ether gave the acid (XVI; R = R′ = H) (9 mg.), m. p. and mixed m. p. 208—209° (correct infrared spectrum). When the reaction was conducted at room temperature for 20 hr. in 0·1N-sodium hydroxide only starting material was recovered.

1,2,3,4,10α,11-*Hexahydro*-1β,11α-*dimethyl*-9-*oxofluorene*-1α-*carboxylic Acid* (XVII).—The acid (VI; R = H) (50 mg.) and lead tetra-acetate (82 mg., 1·1 equiv.) were heated in acetic acid (6 ml.) at 65—70° for 1 hr. The solution was diluted with water and extracted with ether. Chromatography of the recovered gum on silica gel (3 g.) in benzene–ether (9 : 1) gave 1,2,3,4,10α,11-hexahydro-1β,11α-dimethyl-9-oxofluorene-1α-carboxylic acid (XVII) (33 mg.) in needles, m. p. 129—130° (from ether–light petroleum) (Found: C, 74·4; H, 7·0. Calc. for $C_{16}H_{18}O_3$: C, 74·4; H, 7·0%), $\lambda_{max.}$ 248, 293 mμ (log ε 3·93, 3·28 respectively), $\nu_{max.}$ 3400—2500 (broad), 1716 (OH and CO of CO_2H), 1699 (conjugated CO in 5-ring), 1604 cm.$^{-1}$ (aromatic ring). Ohta [7] gives m. p. 130—131°, $\nu_{max.}$ 1695, 1686 cm.$^{-1}$.

Oxidation of Methyl Podocarpa-5,7,13(14)-*trien*-15-*oate by Chromic Oxide*.—The ester (1 g.) in acetic acid (10 ml.) at 60° was treated dropwise with chromic oxide (2 g.) in acetic acid (10 ml.) and water (2 ml.). The mixture was heated at 80° for 7·5 hr. and kept at room temperature for a further 18 hr. After addition of methanol and evaporation *in vacuo*, the residue was diluted with water (50 ml.) and extracted with ether. The ether extract was washed with 2N-sodium carbonate and evaporated, giving a mixture of yellow (A) and colourless (B) prisms. These were separated manually, since fractional crystallisation was difficult. The yellow prisms (A) (350 mg.) were crystallised from benzene and then benzene–light petroleum, giving *methyl* 11-*hydroxy*-9,10-*dioxopodocarpa*-5,7,13(14)-*trien*-15-*oate* (VII; R = H, R′ = CO_2Me) (270 mg., 23%), m. p. 223—226°, $[\alpha]_D^{22}$ +345° (*c* 0·7 in $CHCl_3$) (Found: C, 68·4; H, 6·4; OMe, 9·7. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·4; OMe, 9·9%), $\nu_{max.}$ 3315 (bonded OH), 1739, 1685 (bonded ester and 9,10-diketone C=O), 1598 cm.$^{-1}$ (aromatic ring), or (in CCl_4, dilute solution) 3297 (bonded OH), 1736 (10-ketone CO), 1694 cm.$^{-1}$ (bonded ester and 9-ketone C=O), $\lambda_{max.}$ 285, 442 mμ (log ε 3·83, 1·70 respectively). On addition of 2 drops of 3N-sodium hydroxide the maximum at 285 mμ rapidly decreased whilst the end-absorption below 250 mμ increased, until after 4 hr. no maximum could be detected between 220 and 310 mμ.

Ohta and Ohmori [5] give m. p. 201—203° for their oxidation product of methyl podocarpa-5,7,13(14)-trien-15-oate. The m. p. of the ester (VII; R = H, R′ = CO_2Me) was not depressed

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on admixture with an authentic specimen kindly provided by Dr. Ohta, and the infrared spectra were identical for both solutions and the solid state. The difference in m. p. is ascribed to dimorphism.

The diketo-ester (VII; R = H, R′ = CO_2Me) was stable to hot dilute hydrochloric acid. The *quinoxaline derivative* formed plates, m. p. 188—189° (Found: C, 73·8; H, 6·2. $C_{24}H_{24}N_2O_3$ requires C, 74·2; H, 6·2%), $\nu_{max.}$ 3342 (bonded OH), 1685 cm.$^{-1}$ (bonded ester CO). It gave a yellow colour, which rapidly darkened, with concentrated sulphuric acid.

The colourless prisms (B) crystallised from methanol, to give the acid (X; R = H), m. p. 150—152°, identical (mixed m. p. and infrared spectra) with the material obtained from the acid fraction (below).

Acidification of the sodium carbonate extract followed by extraction with ether and recovery gave methyl 3-*o*-carboxyphenyl-1β,3β-dimethyl-2-oxocyclohexanecarboxylate (lactol form; X; R = H) (365 mg., 33%) as prisms, m. p. 150—152°, $[\alpha]_D^{27}$ −8·3° (*c* 0·9) (Found: C, 67·2; H, 6·8; OMe, 10·9. Calc. for $C_{17}H_{20}O_5$: C, 67·1; H, 6·6; OMe, 10·2%), $\nu_{max.}$ 3425 (OH), 1730 (ester and δ-lactone C=O), 1608 cm.$^{-1}$ (aromatic ring). Ohta and Ohmori [5] give m. p. 151—152°, $[\alpha]_D^{25}$ −8·4° (*c* 2·4).

Oxidation of the Diketo-ester (VII; R = H, R′ = CO_2Me).—The diketo-ester (VII; R = H) (12 mg.) in acetic acid (0·5 ml.) was treated with chromic oxide (9 mg.) in acetic acid (0·5 ml.) and water (0·15 ml.). Heating at 80° for 5·5 hr., and working up as in the previous experiment, gave a gum (10 mg.) which crystallised from methanol in prisms, m. p. 149—150·5°, of the acid (X; R = H). Only starting material was recovered when the reaction was performed at 60° for 7 hr.

Action of Alkali on the Diketo-ester (VII; R = H, R′ = CO_2Me).—The diketo-ester (VII; R = H, R′ = CO_2Me) (52 mg.) in 3N-sodium hydroxide (15 ml.) was heated under reflux for 1 hr., in a nitrogen atmosphere. The cooled solution was extracted with ether, acidified, and again extracted with ether, giving, on recovery, a gum (41 mg.) which crystallised from methanol in prisms (10 mg.), m. p. 221—222°, $[\alpha]_D^{24}$ −10·8° (*c* 0·4 in $CHCl_3$), of 1,2,3,6,7,11b-*hexahydro*-4,11b-*dimethyl*-6,7-*dioxodibenz*[b,d]*oxepin* (VIII) (Found: C, 75·0, 75·3; H, 6·3, 6·1. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%), $\lambda_{max.}$ 202, 260, 290 mμ (log ε 4·18, 4·03, 3·96 respectively), $\nu_{max.}$ 1803 (enol lactone CO), 1678 (conjugated CO), 1659 (C=C), 1600 cm.$^{-1}$ (aromatic ring). It liberated carbon monoxide when heated with phosphoric acid (detected by the production of molybdenum blue with phosphomolybdic acid [13]).

When barium hydroxide was used instead of sodium hydroxide for the hydrolysis of the ester a precipitate of barium carbonate was obtained.

Oxidation of Methyl Abieta-5,7,13(14)-*trien*-15-*oate*.—To the ester (1 g.) in acetic acid (10 ml.) at 80° was added dropwise chromic oxide (2 g.) in acetic acid (10 ml.) and water (2·5 ml.). The solution was heated at 80° for 5·5 hr. and kept at room temperature for 18 hr. The solution was worked up as in previous oxidations, and was separated into yellow gummy acidic (200 mg.) and yellow gummy neutral (722 mg.) fractions by extraction with N-sodium hydroxide.

The acid fraction crystallised from methanol, giving *methyl* 3-(4-*acetyl*-2-*carboxyphenyl*)-1β,3β-*dimethyl*-2-*oxocyclohexanecarboxylate* (lactol form; X; R = Ac) (128 mg.), prisms, m. p. 225—227° (changing to plates above 215°), $[\alpha]_D^{24}$ −59·0° (*c* 0·5 in $CHCl_3$) (Found: C, 66·2, 66·2; H, 6·6, 6·4. $C_{19}H_{22}O_6$ requires C, 65·9; H, 6·4%), $\nu_{max.}$ 3335 (OH), 1723 (ester and δ-lactone CO), 1691 (conjugated CO), 1609 cm.$^{-1}$ (aromatic ring), $\lambda_{max.}$ 225, 245, 291·5, 301 mμ (log ε 4·47, 4·03, 3·04, 3·02 respectively) changing to 215, 255, ~290—293 mμ (log ε 4·29, 4·09, 3·25 respectively) on addition of 2 drops of 3N-sodium hydroxide. It gave a positive iodoform reaction, a red colour with sodium nitroprusside, and on treatment with *o*-nitrobenzaldehyde a substituted indigo.[14]

The amorphous *dinitrophenylhydrazone*, m. p. 256—257° (decomp.), was precipitated from benzene with light petroleum (Found: C, 56·8; H, 5·5. $C_{25}H_{26}N_4O_9$ requires C, 57·0; H, 5·0%).

The neutral fraction was chromatographed on silica gel (20 g.), and the column was eluted with benzene. A yellow band (a) moved rapidly down the column and gave a yellow gum (125 mg.) on recovery. This was distilled at 110—120° (bath)/1·5 × 10^{-4} mm., giving *methyl* 11-*hydroxy*-9,10-*dioxoabieta*-5,7,13(14)-*trien*-15-*oate* (VII; R = Pr^i, R′ = CO_2Me) as a yellow oil (Found: C, 70·7; H, 7·7. $C_{21}H_{26}O_5$ requires C, 70·4; H, 7·3%), $\nu_{max.}$ (in CCl_4) 3320 (bonded OH), 1737 (10-ketone CO), 1699s cm.$^{-1}$ (bonded ester and 9-ketone CO), $\lambda_{max.}$ 258, 291, 450 mμ

[13] Feigl, "Spot Tests in Organic Analysis," Elsevier, Amsterdam, 5th edn., p. 327.
[14] Ref. 13, p. 224.

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(log ε 3·61, 3·67, 1·41 respectively) changed to 250 mμ (log ε 3·77) on addition of 2 drops of 3N-sodium hydroxide.

Continued elution of the column with 50 ml. portions of benzene–ether gave two yellow gummy fractions (benzene–ether ratio and fraction weights in parentheses).

Fraction (b) (9 : 1, 430 mg.), on rechromatography on grade II neutral alumina (40 g.), and elution with benzene–ether in ultraviolet light, gave the following fractions: (i), a blue band (benzene; 144 mg.), intractable gum, (ii) a yellow band (9 : 1; 77 mg.), yellow intractable gum, (iii) (9 : 1; 59 mg.), a yellow gum which deposited colourless prisms of methyl 7-acetyl-1,2,3,4,9,10,11α,12-octahydro-1β,12β-dimethyl-9-oxophenanthrene-1α-carboxylate (XIII), m. p. 142—143°, $[\alpha]_D^{24}$ +30·8° (*c* 1·9 in $CHCl_3$) (Found: C, 73·5; H, 7·4. Calc. for $C_{20}H_{24}O_4$: C, 73·1; H, 7·4%), $\nu_{max.}$ 1723 (ester CO), 1684 (conjugated CO), 1603 cm.$^{-1}$ (aromatic ring) {Ritchie *et al.*[10] give m. p. 144—145°, $[\alpha]_D^{22}$ +30·8° (*c* 2·0 in $CHCl_3$)}, (iv) (3 : 1; 21 mg.), an intractable gum, (v) (1 : 1; 8 mg.) an intractable gum, and (vi) (ether; 8 mg.) a yellow gum depositing yellow prismatic needles, m. p. 135—141°, $\nu_{max.}$ 3300 (OH), 1738, 1691, 1654 (C=O), 1603, 1566 cm.$^{-1}$ (aromatic ring), $\lambda_{max.}$ 243, ~282—287 mμ (log $E_{1\,cm.}^{1\%}$ 2·68, 2·12 respectively).

Fraction (c) (4 : 1; 81 mg.), a yellow intractable gum, was rechromatographed on silica gel (5 g.) and eluted with 10 ml. portions of benzene–ether (19 : 1). After a series of intractable gums (35 mg.) had been eluted, fractions 10—15 crystallised from methanol in prisms (29 mg.), m. p. 140—142°, of the ketone (XIII) (infrared spectrum).

We are indebted to Dr. J. R. Bartels-Keith and Mr. D. Brookes for the infrared spectra and to Mr. H. G. Hemming for the biological tests.

Akers Research Laboratories, Imperial Chemical Industries Limited,
The Frythe, Welwyn, Herts. [*Received, August 5th*, 1960.]

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224. *Infrared Spectra and the Stabilities of Chelate Metal–Ethylenediamine Complexes.*

By D. B. Powell and N. Sheppard.

Infrared absorption bands due to NH_2 rocking and metal–nitrogen stretching frequencies of metal–ethylenediamine co-ordination complexes are correlated with the stability of the complexes, irrespective of whether the spectra are of type A or type B. *X*-Ray evidence, published elsewhere, has shown that type B spectra do not correspond to a planar *cis*-configuration of the ligand.

It has been noted[1] that the infrared spectra of some chelate metal–ethylenediamine complexes fall into two classes, A and B, and that this classification can be made regardless of the overall symmetry of the complex (octahedral, square-planar, or tetrahedral). It was suggested, as a possible cause of the difference, that in compounds giving type A spectra the ligand adopts the *gauche* conformation, giving a non-planar 5-membered ring, whereas in those giving type B spectra the ligand has the *cis*-configuration, corresponding to a planar ring. However, it was pointed out that a preliminary *X*-ray study had given an indication that $[Ni\ en_3]^{2+}$ (en = ethylenediamine), which gave a type B spectrum, has a non-planar 5-membered ring;[2] we have since found that a more detailed *X*-ray study has been made[3] of another ion with a type B spectrum, $[Cu\ en_2]^{2+}$, and this leaves no doubt that it has non-planar rings with near-*gauche* conformations. Our suggested explanation for the difference between type A and type B spectra must now be abandoned.

In a detailed investigation of some of the spectra we have also found their appearance to be affected in part by hydrogen-bonding between NH and the anion. This is particularly true of the spectra of the $[Pt\ en]_2^{2+}$ and $[Pd\ en_2]^{2+}$ ions: the point is considered in more

[1] Powell and Sheppard, *J.*, 1959, 791.
[2] Watanabe and Atoji, *Science (Japan)*, 1951, **21**, 301; *Chem. Abs.*, 1951, **45**, 9982.
[3] Scouloudi, *Acta Cryst.*, 1953, **6**, 651.

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detail in another paper.[4] However, hydrogen-bonding effects can be minimised by choosing a large complex anion,[5] so we now present spectral data for the tetrachloroplatinates(II) of a number of the ethylenediamine complexes. Without complications due to hydrogen bonding, it is now more apparent than previously that there is good correlation between certain features of the whole family of spectra, whether of type A or of type B, and the general stability of the complexes. These features of continuity occur despite the fact that we have still been able to classify all the spectra so far obtained as

Frequencies of δNH_2 *rocking and* $\nu M{-}N$ *vibrations* ($cm.^{-1}$), *and stabilities of metal–ethylenediamine complexes.*

Metal	log $k_{average}$	log K_1	Spectrum type	δNH_2 rock		$\gamma M{-}N$
Pt(II)	$\beta_2/2$ = ?	?	A	795	780	583
Rh(III)	$\beta_3/3$ = ?	?	A	783	773	580
Co(III)	$\beta_3/3$ = 16·3 [a]	18·7 [b]	A	782	770	585
Pd(II)	$\beta_2/2$ = 13·5 [c]	?	A	765	750	573
Cr(III)	$\beta_3/3$ = ?	?	A	726	708	567
Hg(II)	$\beta_2/2$ = 11·7 [d]	12·1 [c]	B	727	695	?
Cu(II)	$\beta_2/2$ = 9·8 [c]	10·55 [c]	B	705sh	694	538
Ni(II)	$\beta_3/3$ = 6·0 [c]	7·52 [c]	B	653	640sh	515
Co(II)	$\beta_3/3$ = 4·6 [c]	5·89 [c]	B	635	620sh	502
Zn(II)	$\beta_3/3$ = 4·0 [c]	5·71 [c]	B	620	598	478
Cd(II)	$\beta_3/3$ = 4·0 [c]	5·47 [c]	B	622	599	478

[a] Bjerrum, "Metal–Amine Formation," P. Haase and Son, Copenhagen, 1941. [b] Bjerrum and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265. [c] Mellor and Maley, *Nature*, 1948, **161**, 436. [d] Bjerrum, *Chem. Rev.*, 1950, **46**, 381. [e] Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334.

type A or type B on grounds of the patterns of intensities of bands in the 1200—1000 $cm.^{-1}$ region. However, it now seems possible that spectra of intermediate type may be found later.

The spectra of a typical range of the complexes are shown in the Figure, in the general order of decreasing stability (a—h). The sequence from mercury(II) to zinc(II) is based on numerical stability constants.[6] The figures given here have been based on results obtained, as far as possible, under comparable conditions of temperature and concentration. Log $k_{average}$ is taken as the logarithm of the overall stability constant (log β_n) divided by the number (n) of groups bound to the metal ion in the usual complex. In some cases there is uncertainty as to how ethylenediamine groups are uniformly bound in the complex, and so, in addition, where available, the figures for the first successive stability constants are also given. For the more stable complexes, actual stability constants are only available for cobalt(III) and palladium(II). On general chemical grounds there is little doubt that the platinum(II) and rhodium(III) complexes are comparable in stability with cobalt(III), and that those of chromium(III) and palladium(II) are rather less stable, but the exact order is uncertain. The spectra from mercury(II) to zinc(II) are of type B, *i.e.* they show an outstandingly strong band near 1000 $cm.^{-1}$. The others, of more stable complexes, are of type A.

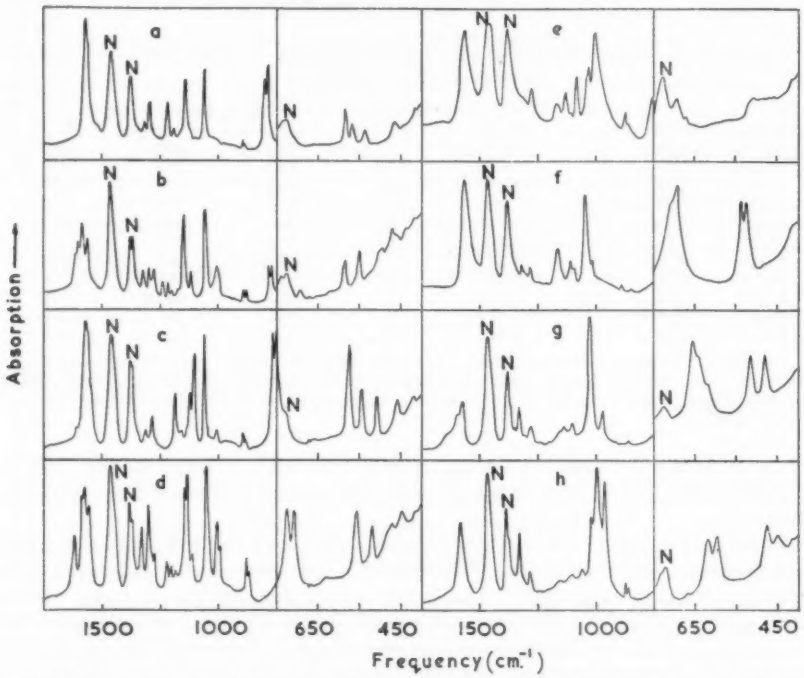
The most interesting features of continuity which follow through the whole series of spectra, are a series of well-defined bands varying in position from about 800 $cm.^{-1}$ in the spectra of the most stable complexes to near 600 $cm.^{-1}$ in the spectrum of the least stable complex ion, $[Zn\ en_2]^{2+}$. These bands are caused principally by NH_2 rocking vibrations. Another sequence of bands, which may be assigned to metal–nitrogen bond stretching, also show regular frequency changes from about 585 to 478 $cm.^{-1}$ in the same series of complexes. These assignments are discussed in detail elsewhere.[4]

These bands are listed in detail in the Table for all the complexes examined, including

[4] Powell and Sheppard, *Spectrochim. Acta*, in the press.
[5] Ebsworth and Sheppard, *Spectrochim. Acta*, 1959, **13**, 261.
[6] Sutton *et al.*, "Stability Constants," *Chem. Soc. Spec. Publ.* No. 13, 1958.

some not shown in the Figure. It may be seen that they are correlated successfully with stability data for the complexes, although it is understood that other factors than the strength of metal–nitrogen bonding must contribute to the stability of these ions in solution.

Infrared spectra of metal–ethylenediamine complexes as tetrachloroplatinates(II); *range* 1750—400 *cm.*$^{-1}$; *Nujol dispersions* (*Nujol peaks marked* N).



(a) Pt(II); (b) Co(III); (c) Pd(II); (d) Cr(III); (e) Hg(II); (f) Cu(II); (g) Ni(II); (h) Zn(II).

However in a study of the complex ammines,[7] similar regularities were found between the NH_3 deformation and metal–nitrogen stretching frequencies, and the general order of stability of the complexes.

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(N. S.) University Chemical Laboratory,
Lensfield Road, Cambridge.

[*Received, September 8th*, 1960.]

[7] Powell and Sheppard, *J.*, 1956, 3108.

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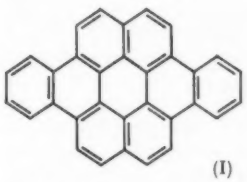
225. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part V.*[1] 1,2:7,8-*Dibenzocoronene.*

By J. Monteath Robertson and James Trotter.

Crystals of 1,2:7,8-dibenzocoronene are monoclinic, with four molecules in a unit cell of dimensions $a = 22{\cdot}83$, $b = 5{\cdot}22$, $c = 15{\cdot}77$ Å, $\beta = 103{\cdot}9°$, space group $C2/c$. All the crystals examined have been twinned on (100). The structure has been determined from normal and generalised projections along the b-axis. The carbon skeleton of the molecule is completely planar, but there is evidence that some of the hydrogen atoms are displaced from this aromatic plane. Details of the molecular dimensions and of the intermolecular separations have been obtained.

A detailed X-ray investigation of the crystal and molecular structure of 1,2:7,8-dibenzocoronene (I) has been undertaken to obtain an accurate account of the dimensions of the molecule. Although partial three-dimensional data have been used to give an independent estimate of all three positional parameters for each carbon atom, the accuracy of the results is limited by the paucity of results obtained from the rather poor-quality twinned crystals. The bond lengths have nevertheless been determined with sufficient accuracy to allow some comparison to be made with the bond distances in related molecules.



(I)

Experimental

Crystals of 1,2:7,8-dibenzocoronene, obtained by crystallisation from 1-methylnaphthalene followed by sublimation in a high vacuum, were yellow needles elongated along the b-axis. The density was determined by flotation in aqueous potassium iodide. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the b-axis, and $h0l$, $h1l$, and $h2l$ Weissenberg films. The Weissenberg photographs indicated clearly that the crystals were twinned on (100), and although several specimens were examined, a single crystal could not be obtained. However the photographs could be readily interpreted and indexed.

The crystal data were: 1,2:7,8-Dibenzocoronene, $C_{32}H_{16}$; M, 400·4; m. p. 496—499°. Monoclinic, $a = 22{\cdot}83 \pm 0{\cdot}06$, $b = 5{\cdot}22 \pm 0{\cdot}01$, $c = 15{\cdot}77 \pm 0{\cdot}05$ Å, $\beta = 103{\cdot}9° \pm 0{\cdot}3°$. Volume of the unit cell = 1824·3 Å^3. d calc. (with $Z = 4$) = 1·449, measured = 1·457 g. cm.$^{-3}$. Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 7{\cdot}65$ cm.$^{-1}$. Total number of electrons per unit cell = $F(000) = 832$. Absent spectra: hkl when $(h + k)$ is odd, $h0l$ when l is odd. Space group is Cc–C_s^4 or $C2/c$–C_{2h}^6.

The intensities of the $h0l$ and $h1l$ reflexions were recorded on Weissenberg films for a crystal rotating about the b-axis, with Cu-K_α radiation, the equi-inclination method being used for the $h1l$ layer. The multiple-film technique [2] was used to correlate strong and weak reflexions. The range of intensities measured was about 2000 to 1 for the $h0l$ reflexions and 7000 to 1 for the $h1l$ reflexions, the estimates being made visually. There were only a few cases where reflexions from different parts of the twinned crystal overlapped on the films, so that indexing and intensity estimation were straightforward for most of the reflexions. In addition it was possible, by measuring intensities of reflexions from both parts of the twin, to obtain reliable values for the intensities even for those cases where overlap occurred.

The cross-section of the crystal normal to the b-axis was 0·11 × 0·09 mm., and no absorption corrections were considered necessary. The structure amplitudes were derived by the usual formulæ for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. 69 independent $h0l$ reflexions and 188 $h1l$ reflexions were observed, representing 30% and 44% respectively of the possible number observable under the experimental conditions.

[1] Part IV, *J.*, 1959, 2623.
[2] Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

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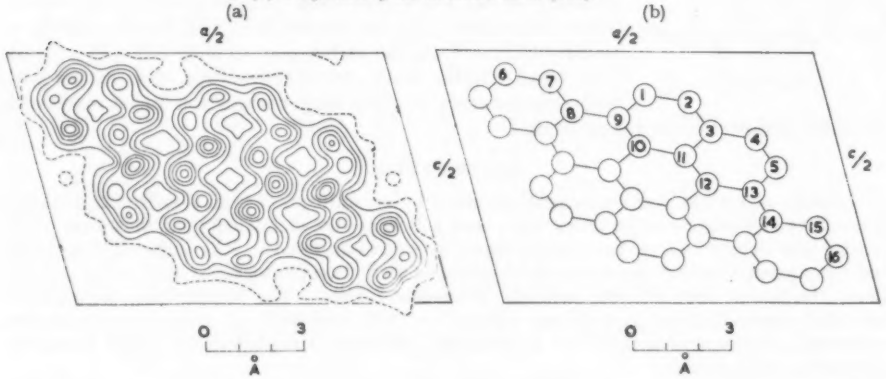
Structure Analysis.—[010] *Projection.* Since it seemed probable that all the atoms in the molecule would be well resolved in the projection along the short *b*-axis, this projection was considered initially. Examination of the *h*0*l* weighted reciprocal lattice revealed regions of strong intensity among the higher-order reflexions, and the positions of these regions indicated clearly the hexagonal symmetry of the Fourier transform of the aromatic rings. The following high-order planes, which correspond approximately to the 1·2 Å spacings of the aromatic six-membered rings, have large structure amplitudes: (18,0,6), (18,0,4), ($\bar{1}\bar{4}$,0,14), ($\bar{1}\bar{4}$,0,12), (4,0,18), and (2,0,18). The orientation of one of the six-membered rings in the molecule was readily deduced by transforming this hexagon in the weighted reciprocal lattice into real space. This orientation was further checked by using a second set of intense reflexions, corresponding to the 2·1 Å spacings in the aromatic rings: ($\bar{1}\bar{0}$,0,2), ($\bar{1}\bar{2}$,0,2), ($\bar{1}\bar{0}$,0,4), ($\bar{4}$,0,10), ($\bar{2}$,0,10), (606), (608), (808). By assuming that all the rings in the molecule had similar dimensions, three possible orientations for the whole molecule were deduced.

A choice between these three orientations was then made from a consideration of the packing of the molecules in the unit cell. Since the cell contains four molecules, which are probably

FIG. 1. (a) *Electron-density projection along the b-axis. Contours at intervals of* 1 eÅ^{-2}, *with the one-electron line broken.*
(b) *Projection of the structure on to* (010).



planar and centrosymmetrical, it seemed likely that the true space group was the centrosymmetrical one $C2/c$. When each molecule was placed on a centre of symmetry in this space group, only one of the three possible orientations could be fitted into the cell with the usual intermolecular separations. In addition the packing considerations also indicated that the molecule could not be accommodated on the centre of symmetry at (0,0,0), but was situated on the centre at ($\frac{1}{4}$,$\frac{1}{4}$,0).

Structure factors were calculated for all the observed *h*0*l* reflexions, with the scattering curve for carbon of Berghuis *et al.*,[3] corrected for thermal vibration with $B = 4{\cdot}2$ Å^2 for all the atoms. The discrepancy between measured and calculated structure factors was 19·0%, so that there was no doubt that this structure, deduced from Fourier transform and packing considerations, was correct.

A Fourier series was then summed, measured structure amplitudes with calculated signs being used as coefficients. On the resulting electron-density map (Fig. 1) all the carbon atoms were well resolved. Further refinement proceeded by computing successive difference syntheses, with ($F_o - F_c$) as coefficients, and altering the positional and isotropic temperature parameters to minimise the slopes and difference electron-densities at the atomic centres. One cycle reduced the discrepany factor to 13·6%, and a second cycle to 11·9%. The final measured and calculated structure factors are listed in Table 3. Throughout the refinement there were no sign changes, so that Fig. 1 represents the final electron-density projection along the *b*-axis.

y-*Co-ordinates.* No resolution of the individual atoms in the molecule could be expected in

[3] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

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projections down the *a*- or *c*-crystal axes, and the problem of finding the *y*-co-ordinates was therefore approached by considering the *h*1*l* structure factors.

Approximate *y*-co-ordinates were easily deduced from a consideration of the bond lengths projected on (010), and these trial co-ordinates were then refined by use of difference generalised projections.[4] By using both cosine and sine series simultaneously it is possible to refine all three positional parameters *x*, *y*, *z*, and the isotropic temperature parameters, *B*, at the same time.

Structure factors were calculated for the *h*1*l* reflexions by using the *x*, *z*, and *B* parameters from the *h*0*l* refinement, and the trial *y*-co-ordinates. The discrepancy factor was 23·6%. Refinement proceeded by computing cosine and sine difference generalised projections. The resulting electron-density maps indicated that no significant changes in *x*, *z*, and *B* parameters were required. New *y*-co-ordinates (y_0) were obtained from the relation:

$$\sin 2\pi(y_0 - y_c) = \frac{1}{\sigma_{1,0}} \{S_1{}^D \cos 2\pi y_c - C_1{}^D \sin 2\pi y_c\}$$

where y_c are the co-ordinates used in the previous structure factor calculation, $S_1{}^D$ and $C_1{}^D$ are the values of the sine and cosine difference generalised projections at the atomic positions, and $\sigma_{1,0}$ is the generalised density (approximately equal to the electron density in the *h*0*l* projection). The maximum shift in *y*-co-ordinate was 0·05 Å. Structure factors were recalculated with the revised co-ordinates, and the discrepancy factor was 17·3%. A second set of difference generalised projections was calculated, but no further significant changes in *y*-co-ordinates were indicated. The final measured and calculated *h*1*l* structure factors are included in Table 3. Cosine and sine generalised projections, computed from measured structure amplitudes and calculated signs, are shown in Fig. 2. These maps represent projections of the structure on to (010) with the electron density in the *j*th atom multiplied by cos $2\pi y_j$ and sin $2\pi y_j$ respectively.

TABLE 1. *Final positional and temperature parameters, and deviations* (Δ) *from the mean plane.*

Atom *	*x*	*y*	*z*	*X′*	*Y*	*Z′*	*B* (Å²)	Δ (Å)
C 1	0·2604	0·775	0·1641	5·771	4·046	1·161	4·5	+0·009
2	0·3175	0·770	0·1504	7·036	4·019	0·632	4·5	+0·020
3	0·3351	0·607	0·0920	7·426	3·169	−0·386	4·5	−0·013
4	0·3929	0·600	0·0785	8·707	3·132	−0·915	4·5	+0·008
5	0·4098	0·430	0·0208	9·082	2·245	−1·918	4·5	+0·006
6	0·0837	0·769	0·2020	1·855	4·014	2·727	4·5	+0·004
7	0·1405	0·776	0·1884	3·114	4·051	2·201	4·5	−0·028
8	0·1589	0·601	0·1321	3·521	3·137	1·212	4·2	+0·007
9	0·2170	0·599	0·1170	4·809	3·127	0·656	4·2	−0·007
10	0·2341	0·430	0·0595	5·188	2·245	−0·345	4·0	−0·010
11	0·2919	0·427	0·0427	6·469	2·229	−0·926	4·0	−0·038
12	0·3099	0·248	−0·0135	6·868	1·295	−1·911	4·0	+0·009
13	0·3680	0·244	−0·0285	8·155	1·274	−2·466	4·2	+0·004
14	0·3842	0·077	−0·0862	8·514	0·402	−3·465	4·2	−0·010
15	0·4434	0·077	−0·0978	9·826	0·402	−3·972	4·5	+0·011
16	0·4598	−0·091	−0·1574	10·190	−0·475	−5·002	4·5	−0·020
Molecular centre	0·2500	0·250	0	5·540	1·305	−1·370	—	0

* Cf. Fig. 4.

TABLE 2. *Orientation of the molecule in the crystal.*

$\chi_L = 47° 00'$	$\chi_M = 48° 11'$	$\chi_N = 106° 31'$
$\psi_L = 111° 33'$	$\psi_M = 48° 47'$	$\psi_N = 48° 34'$
$\omega_L = 129° 14'$	$\omega_M = 69° 38'$	$\omega_N = 133° 56'$

Co-ordinates, molecular dimensions, and orientation. The final positional and temperature parameters of the carbon atoms are listed in Table 1, *x*, *y*, and *z* being co-ordinates referred to the monoclinic crystal axes and expressed as fractions of the unit-cell edges, and *X′*, *Y*, and *Z′* co-ordinates in Ångström units referred to orthogonal axes *a′*, *b*, and *c*.

[4] Rossmann and Shearer, *Acta Cryst.*, 1958, **11**, 829.

FIG. 2. (a) *Cosine and* (b) *sine generalised projections using the hll data. Contours at intervals of* 1 eÅ^{-2}, *negative contours broken, zero contours omitted.*

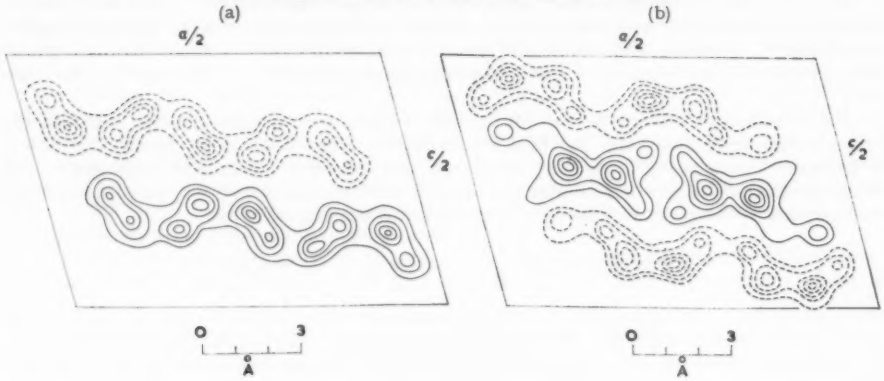


FIG. 3. (a) *Measured bond lengths* (Å) *and valency angles* (degrees). (b) *Mean bond lengths and valency angles.*

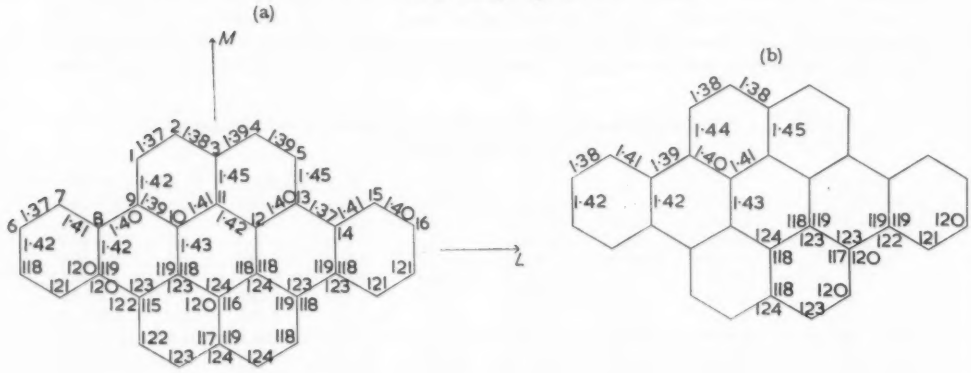


FIG. 4. *Normal projection of two parallel molecules.*

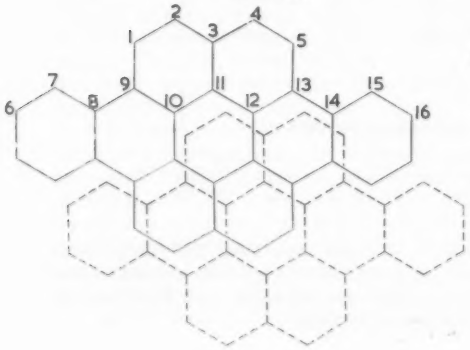
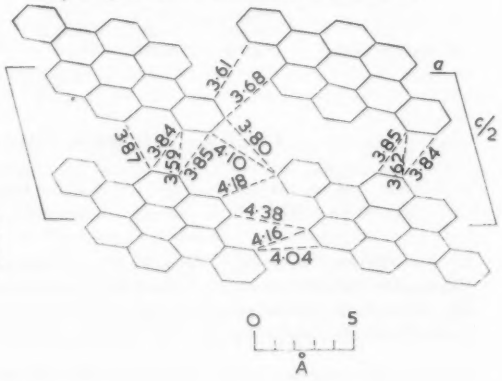


FIG. 5. *Projection of the structure on to* (010), *showing the shorter intermolecular distances.*



The equation of the mean molecular plane is

$$0{\cdot}2843X' - 0{\cdot}6615Y + 0{\cdot}6939Z' + 0{\cdot}2396 = 0$$

and the deviations of the atoms from this plane are listed in final column of Table 1.

The bond lengths and valency angles in the molecule, calculated from the co-ordinates of Table 1, are shown in Fig. 3(a). These values indicated that the symmetry of the molecule did not differ significantly from *mmm*, and the mean values of the bond lengths and valency angles are shown in Fig. 3(b).

The orientation of the molecule in the crystal is given in Table 2, where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_N; and χ_N, ψ_N, ω_N are the angles which the molecular axes L, M (see Fig. 3a), and the plane normal N make with the orthogonal axes a', b, and c. L was taken through the molecular centre and the mid-point of bond 6′–16, and M through the molecular centre and atom 3 (for numbering used see Fig. 4). L, M, and N are thus not accurately mutually perpendicular, the angles being $\widehat{LM} = 90° 25'$, $\widehat{MN} = 89° 43'$, $\widehat{LN} = 89° 53'$. The angle between the plane of the molecule and the (010) plane, which is expressed as ψ_N, the angle between the normal to the molecular plane and the b-axis, is 48·6°. For coronene [5] the corresponding angle is 43·7°.

TABLE 3. *Measured and calculated structure factors (one-half absolute scale).*

h k l	|F$_o$|	F$_c$	h k l	|F$_o$|	F$_c$	h k l	|F$_o$|	F$_c$	h k l	|F$_o$|	F$_c$	h k l	|F$_o$|	F$_c$	h k l	|F$_o$|	F$_c$	h k l	|F$_o$|	F$_c$
2 0 0	79·4	−79·2	$\bar{6}$ 0 8	6·2	+6·3	5 1 1	19·6	−18·2	1 1 4	90·1	+91·6	7 1 7	2·7	+6·1	$\bar{11}$ 1 11	4·4	−6·5	
4	48·3	−50·2	$\bar{4}$	9·4	−6·1	7	7·5	+9·7	3	1·4	−4·4	17	5·5	−8·2	$\bar{3}$	8·3	+5·8	
6	21·7	−21·0	$\bar{2}$	6·6	−6·7	9	2·1	+3·9	5	11·5	+6·3	19	4·8	+7·5	1	4·6	+6·8	
8	7·5	−5·8	0	9·6	−9·3	11	23·8	−20·5	7	39·7	−39·3	$\bar{21}$ 1 8	5·9	+10·6	3	2·5	−5·4	
10	5·6	−3·5	4	8·5	+9·0	13	19·3	+22·5	9	3·4	−4·5	$\bar{17}$	3·7	+4·2	7	15·2	−13·0	
12	2·8	−4·7	6	32·9	+27·7	15	13·7	+10·6	11	3·5	−3·3	$\bar{15}$	11·2	−14·3	9	10·0	+10·6	
$\bar{14}$ 0 2	13·9	−10·8	8	37·5	−40·3	17	21·8	−27·4	17	6·0	−6·7	9	8·4	+7·3	13	4·3	+4·7	
$\bar{12}$	41·1	−46·5	$\bar{14}$ 0 10	7·4	+9·0	19	2·7	+4·4	19	4·6	+8·4	7	3·7	−6·3	$\bar{13}$ 1 12	6·5	+9·3	
$\bar{10}$	53·6	+56·0	$\bar{4}$	45·8	−41·9	$\bar{21}$ 1 2	2·7	−5·6	$\bar{13}$ 1 5	7·4	−6·3	5	20·1	−17·0	9	3·6	+6·2	
$\bar{8}$	11·7	+14·6	$\bar{2}$	25·9	+22·6	$\bar{17}$	3·5	+7·3	$\bar{11}$	28·9	−29·6	$\bar{3}$	20·7	+17·8	$\bar{3}$	6·4	−11·9	
$\bar{4}$	17·3	+21·2	0	6·5	+5·4	$\bar{11}$	6·4	+10·3	9	18·5	+12·6	1	14·3	−10·2	7	5·9	+4·3	
$\bar{2}$	10·2	+10·4	$\bar{8}$	8·4	−5·5	$\bar{9}$	5·1	−5·9	7	6·5	+3·8	3	6·5	+5·0	9	7·0	−6·3	
0	79·1	+78·1	$\bar{18}$ 0 12	9·3	+10·0	7	13·0	−14·3	$\bar{5}$	11·6	+9·2	7	2·3	+3·2	13	4·6	+3·9	
2	77·2	−76·7	$\bar{16}$	13·4	+16·5	$\bar{5}$	12·9	−12·4	$\bar{3}$	11·6	+9·6	17	5·0	+4·4	$\bar{15}$ 1 13	3·7	−5·6	
4	55·7	−51·8	$\bar{14}$	37·8	−36·5	$\bar{3}$	30·3	−34·3	1	5·7	+7·3	19	10·5	−11·7	$\bar{13}$	3·8	+3·6	
6	14·4	−14·6	$\bar{6}$	11·5	−2·4	1	63·5	−62·6	1	30·7	−30·1	$\bar{21}$ 1 9	4·5	+7·7	$\bar{5}$	5·2	+2·9	
8	10·5	−11·6	$\bar{4}$	15·3	−8·4	1	98·5	+96·2	3	23·4	+23·4	$\bar{19}$	7·1	−11·2	$\bar{3}$	15·1	−9·7	
12	9·5	+13·6	$\bar{2}$	20·5	+16·4	3	20·3	+13·0	5	34·3	+28·5	$\bar{17}$	3·7	−9·3	1	9·1	+9·1	
$\bar{16}$ 0 4	6·9	−9·7	0	5·2	+5·0	5	15·2	+10·3	7	34·5	−28·2	$\bar{15}$	21·4	+27·3	1	5·0	−4·4	
$\bar{12}$	11·0	−11·1	2	7·5	−4·8	9	2·2	+5·2	9	4·7	+8·1	$\bar{13}$	2·5	−5·1	3	5·7	+5·5	
$\bar{10}$	48·5	+50·4	$\bar{14}$ 0 14	29·6	−30·9	11	18·8	+15·6	11	3·6	+3·7	9	3·1	−4·8	$\bar{15}$ 1 14	6·3	+6·6	
$\bar{8}$	5·1	−3·2	$\bar{12}$	17·3	+14·0	13	6·3	−6·8	17	2·7	+4·8	$\bar{3}$	15·4	−11·5	$\bar{13}$	5·9	−4·6	
$\bar{4}$	31·4	−34·4	$\bar{10}$	10·9	+8·5	15	6·5	−3·8	$\bar{15}$ 1 6	5·0	+8·1	1	4·2	−4·5	$\bar{3}$	15·4	−11·2	
$\bar{2}$	20·3	−19·8	4 0 16	9·5	+5·4	17	22·1	−25·1	$\bar{13}$	3·1	+0·4	1	6·8	−7·5	1	2·7	−0·9	
0	44·2	−50·6	2 0 18	11·8	−4·5	19	5·3	+9·7	$\bar{11}$	16·6	−14·8	$\bar{3}$	5·0	+6·0	$\bar{3}$	17·9	+15·4	
2	37·8	+39·1	4	23·9	+18·7	21	2·6	+3·1	9	27·6	+23·9	7	3·5	−6·8	5	3·2	−3·5	
4	7·4	+6·7				$\bar{21}$ 1 3	6·5	+11·1	$\bar{5}$	27·6	−22·2	9	6·3	−0·5	$\bar{15}$ 1 15	4·9	+7·5	
6	22·5	−23·3	1 1 0	16·6	−17·1	$\bar{11}$	7·4	+6·1	$\bar{3}$	17·2	+13·3	17	4·1	−2·2	$\bar{3}$	5·6	−2·7	
8	5·3	+8·7	$\bar{3}$	17·3	−15·2	$\bar{9}$	3·7	−2·4	$\bar{3}$	6·1	−6·4	19	10·0	+10·9	1	7·4	+6·6	
14	12·3	+16·5	5	22·3	−22·0	$\bar{5}$	18·6	−15·7	7	29·2	−24·2	$\bar{21}$ 1 10	2·5	+5·2	1	6·3	−3·0	
16	18·8	+16·7	11	36·7	+35·7	$\bar{3}$	25·3	−25·4	11	3·4	+3·2	$\bar{19}$	2·6	−2·0	3	22·6	+17·1	
$\bar{18}$	31·0	−34·9	15	2·8	+4·0	1	64·6	−63·3	17	5·0	+6·5	$\bar{15}$	20·3	−25·6	5	5·9	−6·9	
$\bar{20}$ 0 6	12·2	−16·9	17	12·7	−13·9	1	132·8	−137·0	19	3·6	−4·6	$\bar{13}$	10·1	+9·8	$\bar{15}$ 1 16	3·2	+5·2	
$\bar{16}$	5·0	+5·9	$\bar{23}$ 1 1	3·1	−7·5	3	18·7	+21·6	$\bar{15}$ 1 7	3·9	−7·2	$\bar{11}$	5·4	+5·8	$\bar{13}$	13·7	−12·3	
$\bar{6}$	5·3	−11·6	$\bar{17}$	2·5	+7·1	5	30·4	+30·3	$\bar{11}$	8·5	−8·3	7	3·2	+3·5	3	11·8	+9·5	
$\bar{2}$	3·2	−4·7	$\bar{13}$	2·9	+4·4	7	14·3	−12·6	$\bar{9}$	23·6	+22·1	$\bar{5}$	2·2	+1·4	5	5·7	−6·2	
0	15·8	+15·5	$\bar{11}$	11·1	−9·0	17	13·5	−15·0	7	8·3	+7·5	1	4·0	+4·5	$\bar{15}$ 1 17	2·4	+2·3	
2	13·1	−14·3	$\bar{9}$	11·7	+10·6	19	5·3	+11·6	$\bar{5}$	37·2	+30·8	3	5·9	−6·9	$\bar{13}$	12·4	−11·9	
4	13·3	+13·6	$\bar{7}$	13·2	+15·5	21	3·1	+3·8	$\bar{3}$	35·6	−31·1	7	11·5	+8·9	$\bar{11}$	4·5	+4·2	
6	30·9	+30·7	$\bar{5}$	15·6	−14·7	$\bar{11}$ 1 4	15·4	−15·7	1	9·9	−8·6	9	6·5	−8·9	$\bar{9}$	5·7	+6·1	
8	12·1	−15·9	1	10·5	−17·2	$\bar{9}$	9·3	+10·4	1	20·3	+16·6	19	3·5	−4·6	7	4·7	−5·3	
18	28·6	−29·5	1	16·8	+16·3	$\bar{3}$	14·5	−13·0	3	10·4	−10·7	$\bar{15}$ 1 11	12·5	+14·6	$\bar{13}$ 1 18	4·9	−4·9	
8 0 8	7·1	+10·6	3	3·1	+1·2	1	26·7	−20·7	5	2·0	−4·6	$\bar{13}$	12·8	−14·0	7	5·9	+7·0	

Standard deviations. The standard deviations of the atomic positions were calculated from Cruickshank's formulæ.[6] The mean values for all the atoms are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}012$ Å, so that the standard deviation of the individual bond distances is 0·017 Å. This value may be compared with the root-mean-square deviation of the individual bond lengths from the mean values, for those bonds for which two independent measurements have been made, this value being 0·012 Å. The standard deviations of the mean bond distances are 0·017 Å for those bonds where there is only one measured value, and $0{\cdot}017/\sqrt{2} = 0{\cdot}012$ Å for those bonds where two independent measurements are available.

[5] Robertson and White, *J.*, 1945, 607.
[6] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

Intermolecular distances. All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation *b* is 3·45 Å, but the carbon atoms in contact tend to avoid direct overlap as can be seen from Fig. 4, which shows the normal projection of two parallel molecules. The corresponding perpendicular distance in coronene is 3·40 Å. The shorter lateral contacts are illustrated in Fig. 5.

Discussion

The carbon skeleton of the molecule of 1,2:7,8-dibenzocoronene is completely planar within the limits of experimental error, the maximum deviation of the atoms from the mean plane being 0·038 Å, and the root-mean-square deviation 0·016 Å. There is, however, some indication on the electron-density map (Fig. 1), and on the corresponding difference synthesis, that the hydrogen atoms in the "overcrowded" positions (those bonded to carbons 7, 1, 5, and 15) deviate from the ring diagonals in a manner which suggests that H(7) and H(1) are pushed out of the aromatic plane in opposite directions, and similarly H(5) and H(15). This evidence is of course not very definite, but the possible deviations are in accord with the displacements which might be expected in order to increase non-bonded H · · · H separations of about 1·7 Å in a completely planar model to the usual van der Waals distances.

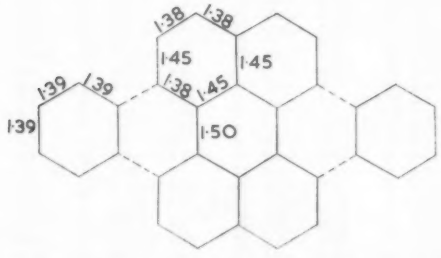


Fig. 6. *Bond lengths in perylene and an o-phenylene group.*

The bond distances in the central portion of the 1,2:7,8-dibenzocoronene molecule (Fig. 3b) are very similar to the corresponding lengths in perylene [7] (Fig. 6), suggesting that, to a first approximation, the molecule might be considered as being built up from perylene by the addition of two *o*-phenylene groups. A shortening of the *peri*-bond from 1·50 to 1·43 Å indicates an increase in aromatic character in that part of the dibenzocoronene molecule in comparison with perylene, but the fact that this distance is not reduced as far as the aromatic value (1·39 Å) supports the molecular formulation suggested by Clar [8] from spectroscopic evidence.

With respect to this and the following paper, the authors thank Dr. E. Clar for the crystal samples, and the Superintendent of the Mathematics Division of the National Physical Laboratory for permission to use the DEUCE programmes developed there by Dr. J. S. Rollett, and one of us (J. T.) is indebted to the University of Glasgow for an I.C.I. Senior Research Fellowship.

Chemistry Department, University of Glasgow. [*Received, September 8th*, 1960.]

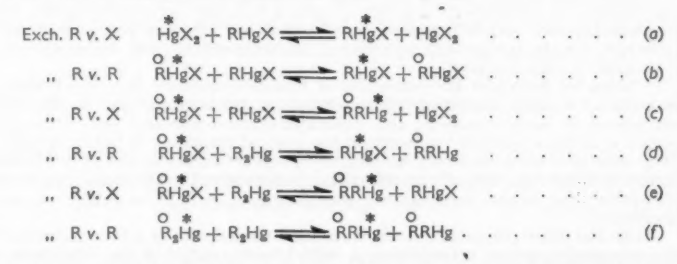
[7] Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.
[8] Clar, Ironside, and Zander, *Tetrahedron*, 1959, **6**, 358.

226. *Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part III.*[1] *Kinetics, Stereochemistry, and Mechanism of the Three-alkyl Mercury-exchange Reaction.*

By H. B. Charman, E. D. Hughes, Sir Christopher Ingold, and F. G. Thorpe.

It is shown that mercury-for-mercury replacement in the reactions of s-butylmercuric bromide, acetate, and nitrate, severally, with di-s-butylmercury in ethanol is the anticipated, but observationally new, three-alkyl substitution, proceeding by the bimolecular electrophilic mechanism S_E2, in which stereochemical configuration is fully preserved. That this three-alkyl electrophilic exchange is indeed under observation, rather than any other process or combination of processes of alkyl-redistribution that might have simulated its stoicheiometry, is shown both by double-labelling, using the labels of optical activity and radioactivity in conjunction and alternatively, and by a study of kinetic form. That the substitution fully preserves configuration is shown both by the polarimetrically followed kinetics, and by the final rotations of products from "spent" runs. That, of the two mechanisms, S_E2 and S_Ei, which are both consistent with both the second-order kinetic form and the retention of configuration, the one actually observed is mechanism S_E2, is shown both by the great increase of rate with increasing ionicity of the substituting agent, and by the positive kinetic effects of added lithium salts, which, lithium bromide not excepted, act broadly according to the ease of their ionic dissociation, and independently of the nature of the s-butylmercuric substituting agent, in the range studied.

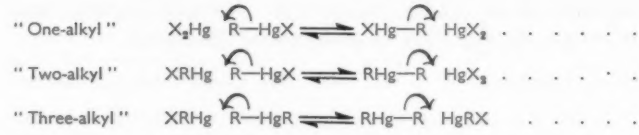
(1) *Introduction to Parts* III—V.—As explained in Part I,[2] we have entered on the study of electrophilic substitution at saturated carbon by way of the redistribution reactions of alkylmercury compounds, because replacement of mercury by mercury allows the stereochemical part of the mechanistic evidence to be presented without the assumptions involved in assigning configurations to the optical isomers with which we deal when one element is being replaced by another. There are six conceivable redistribution reactions, (*a*)—(*f*) below, and we shall be concerned with problems of distinguishing between them, when, either in one step or more than one, several could lead to an identical overall stoicheiometry. The labels on R and Hg are at this stage attached only for clarity: in experimental work one does not always need all of them:


Exch. R v. X
$^{*}HgX_2 + RHgX \rightleftharpoons RHg^{*}X + HgX_2$ (a)
,, R v. R
$^{\circ *}RHgX + RHgX \rightleftharpoons {}^{*}RHgX + {}^{\circ}RHgX$ (b)
,, R v. X
$^{\circ *}RHgX + RHgX \rightleftharpoons {}^{\circ}RRHg^{*} + HgX_2$ (c)
,, R v. R
$^{\circ *}RHgX + R_2Hg \rightleftharpoons {}^{*}RHgX + {}^{\circ}RRHg$ (d)
,, R v. X
$^{\circ *}RHgX + R_2Hg \rightleftharpoons {}^{\circ}RRHg^{*} + RHgX$ (e)
,, R v. R
$^{\circ *}R_2Hg + R_2Hg \rightleftharpoons {}^{\circ}RRHg^{*} + {}^{\circ}RRHg$ (f)

Theoretically, only the redistributions (*a*), (*c*), and (*e*) can be formulated as electrophilic substitutions. These one-, two-, and three-alkyl exchanges, as we call them, are so formulated in (1)—(3) below. However, it is a matter for experimental demonstration whether they all, and they alone, exist as independent processes. The two-alkyl reaction was well known so to do, and, on that foundation, we developed in Part II [1] a study of its kinetics and stereochemistry in correlation. It was mentioned there that the three- and

[1] Part II, Charman, Hughes, and Ingold, *J.*, 1959, 2530.
[2] Charman, Hughes, and Ingold, *J.*, 1959, 2523.

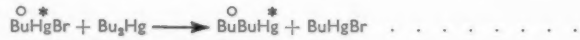
one-alkyl exchanges, on which we now report, had been identified and investigated similarly.[3]



(1) (2) (3)

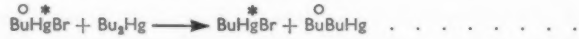
(2) *Three-alkyl Exchange: Identification by Double-labelling.*—No alkylmercury redistribution which might be the three-alkyl exchange has been described before.* Unlike the two-alkyl substitution, whose factors and products are always different, observation of the three-alkyl exchange requires distinctions either between the alkyl groups or between the mercury atoms. Having available optically active s-butylmercuric salts,† we could introduce a label of optical activity on an alkyl group, and follow alkyl exchange with di-s-butylmercury by following movement of the optical label. With s-butylmercuric bromide, for example, such movement does take place at a convenient rate in ethanol at 35°.

Now this result might arise from any of three of the above redistribution reactions, *viz.*, from a single step of reaction (*e*), a single step of reaction (*d*), or a combination of forward and backward steps of the well-known reaction (*c*). A possibility of distinguishing between these alternatives arises, if we introduce additionally a label of radioactivity on one of the mercury atoms, as with ^{203}Hg, and follow alkyl exchange and mercury exchange side by side. This can be seen from the following equations, in which Bu means s-Bu, the degree-sign signifies a label of optical activity, and the asterisk one of radioactivity. In a single step of reaction (*e*),



(4)

one mercury label is transferred, for each alkyl label that is transferred, from one chemical species to the other; *i.e.*, the ratio, mercury-exchange/alkyl-exchange = 1. In a single step of reaction (*d*),



(5)

no mercury label is transferred when an alkyl label is thus transferred; *i.e.*, the ratio, mercury-exchange/alkyl-exchange = 0. In a composition of two steps of reaction (*c*),

* [*Added in proof.*] Except in the preliminary record of this work.[3] But since the present paper was written, a preliminary account of such a reaction between optically active 2-methylhexane-5-mercuric bromide and di(2-methylhexyl-5-)mercury has been given by Reutov and his co-workers.[3a] In both accounts, the method was that of double labelling (*vide infra*), and the conclusions derived by that method were identical.

† Since we described the resolution of butane-2-mercuric (*i.e.*, s-butylmercuric) salts through the mandelate,[4] we have described it through the normal tartrate,[3] and Reutov and Uglova have reported resolutions of both butane-2- and 2-methylhexane-5-mercuric salts through their ethyl tartrates.[5] Jensen *et al.* have recently [6] redescribed the original resolution of butane-2 salts through the mandelate. They refer in a footnote to our account of two years earlier as one of a " partial resolution," omitting to mention that our originally recorded highest rotation of the bromide ($[\alpha]_D^{20}$ −24·0°, c = 5, in acetone) was quite close to the maxima they now give ($[\alpha]_D$ −24·0° to −25·9° in various other polarimetric conditions).

Both the other groups of authors have used their optically active materials to confirm the retention of configuration, which we established, with kinetic control of the conditions, in Part II,[1] in the two-alkyl conversion of a dialkylmercury with mercuric bromide to an alkylmercuric bromide. Reutov and Uglova did this [7] with their 2-methylhexane-5-derivative, and Jensen has now done it,[8] exactly as we did, except that he omits kinetic control, using the butane-2-compound. The optical results (ratios of rotations of factors and products) of these three investigations agree perfectly.

[3] Charman, Thesis, London University, 1958.
[3a] Reutov, Karpov, and Uglova, *Tetrahedron Letters*, 1960, No. 19, 6.
[4] Charman, Hughes, and Ingold, *Chem. and Ind.*, 1958, 1517.
[5] Reutov and Uglova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 757.
[6] Jensen, Whipple, Wedegaertner, and Landgrebe, *J. Amer. Chem. Soc.*, 1960, **82**, 2466.
[7] Reutov and Uglova, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1959, 1691.
[8] Jensen, *J. Amer. Chem. Soc.*, 1960, **82**, 2469.

mercuric bromide would be produced in the first step but consumed in the second, and thus would not enter into the overall stoicheiometry:

$$\left.\begin{array}{l} {}^{\circ}_{*}\mathrm{BuHgBr} + {}^{\circ}_{*}\mathrm{BuHgBr} \longrightarrow {}^{\circ}_{*}\mathrm{Bu_2Hg} + {}^{*}\mathrm{HgBr_2} \\ {}^{*}\mathrm{HgBr_2} + \mathrm{Bu_2Hg} \longrightarrow {}^{*}\mathrm{BuHgBr} + \mathrm{BuHgBr} \end{array}\right\} \quad \ldots\ldots\ldots \quad (6)$$

The net result is that one mercury label is transferred when two alkyl labels are transferred from one chemical form to the other, *i.e.*, that the ratio, mercury-exchange/alkyl-exchange = $\frac{1}{2}$.

We made the twice-labelled alkylmercuric salt by an application of the exchange reaction which forms the subject of the two following papers: optically active s-butylmercuric bromide was brought to equilibrium with radioactive mercuric bromide, so that the resulting s-butylmercuric bromide had become labelled in both ways:

$${}^{\circ}\mathrm{BuHgBr} + {}^{*}\mathrm{HgBr_2} \rightleftharpoons {}^{\circ}_{*}\mathrm{BuHgBr} + \mathrm{HgBr_2}$$

The product had a specific optical rotation (measured, as is done throughout this work, with $l = 2$ dm.) of $[\alpha]_D^{20}$ $-14{\cdot}5°$ ($c = 5$, in acetone), *i.e.*, 60% of the maximum, and a radioactivity, due to ^{203}Hg, which, of course, fell slowly from day to day (the half-life is 46·5 days), but, in concentrations up to 0·1M in acetone, gave counts of the order of 10,000 in periods up to 1 hr. The radioactivity of this initial material was always measured on the same day as that of each timed sample from a kinetic experiment, such as that (run 1) now to be described.

A solution, 0·1M in the twice-labelled s-butylmercuric bromide, and 0·1M in unlabelled di-s-butylmercury, in solvent ethanol, was set at 35°; and, at times up to 65 hours, when 85% of the possible exchange had occurred, samples were taken for measurement of the radioactivity and the optical activity in separated s-butylmercuric bromide. (The change of optical activity was thereafter followed for much longer, for a reason explained in Section 3.) The rate of mercury exchange, as determined by the transfer of radioactivity, was $4{\cdot}4 \times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$. The rate of alkyl exchange, as given by the change of optical activity, was $4{\cdot}6 \times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$. Thus the ratio, mercury-exchange/alkyl-exchange, was 0·96, *i.e.*, unity to within the experimental error.

It follows that the reaction under observation is that of equation (4), *i.e.*, it exemplifies the three-alkyl electrophilic substitution (*e*) or (3)—a new reaction. It cannot be the reaction of equation (5), which would exemplify the non-electrophilic redistribution process (*d*); for that should produce no mercury exchange. The composition, represented in equations (6), of two steps of the known two-alkyl electrophilic substitution (*c*) or (2), is nearly as thoroughly excluded by the above result; and we shall confirm its exclusion, both by a modification of the same method, and by a completely independent method, in Section 4.

It is necessary to understand the meaning of exchange-rate figures, such as those quoted above. The relevant formulæ are included in an Appendix dealing mainly with a more complicated situation than that described above. However, the matter can be appreciated less formally.

In a mixture of constant composition at constant temperature, any exchange, apart from labels, of what we may call an exchangeable " residue," *i.e.*, any atom or group that does exchange, goes on for ever at a constant rate. This zeroth-order rate, k_0, is equal to the measurable *initial* rate of transfer of the residue from a chemical species in which, uniquely, it was originally labelled—the " initial rate of label-transfer," as we may say,—" initial," because it must apply to the period before labelled and unlabelled residues become mixed in the same chemical species. The observable label-transfer in the sense defined will be a first-order process, the ultimately possible extent of which, reckoned as a fraction of the total labelled-residue concentration, is just the ratio of unlabelled to total

residues, *e.g.*, $\frac{1}{2}$ for mercury, and $\frac{2}{3}$ for alkyl, in the above-described experiment. If, at time t, a fraction f of the ultimate amount of transfer has still to occur, the first-order rate-constant for label-transfer will, of course, be $k_1 = -(1/t) \ln f$. By definition, this is the rate, $-df/dt$, at $t = 0$. If now we multiply the " initial rate of label-transfer " in this form by the denominator of the fraction f, *i.e.*, by the concentration of label ultimately transferable—in the above example, by $\frac{1}{2}$ or $\frac{2}{3}$, as the case may be, of the concentration, 0·1M, of the originally labelled compound—we shall have the initial rate in concentration units, $-dc/dt$, at $t = 0$. And this is the constant rate of exchange, k_0, of the residue, apart altogether from labels.

(3) *Stereochemical Course of the Three-alkyl Substitution.*—This is shown, first of all, by the experiment already described. For unless the label of optical activity " stuck " firmly to its alkyl group, while this was being passed about from one chemical species to the other, rates of alkyl exchange, k_0^{Alk}, computed as described from observations of optical activity made at different times during the run, would not be consistent. Good consistency has, however, been obtained in all runs followed by the optical method as illustrated in the Experimental section in Table 8. Most of these runs lack a simultaneously present label of radioactivity, and are reported in summary in this Section and the following one.

Still more forcibly, the firm " sticking " of the optical label is proved by the fact that the final irreducible rotation of the s-butylmercuric bromide recovered from " spent " runs, after periods of the order of 20 half-lives, is one-third of the initial rotation of that substance; and one-third is the ratio of labelled to total alkyl groups. Thus, in the doubly-labelled run described above (run 1), the rotation of the s-butylmercuric bromide, $[\alpha]_D^{20}$ ($c = 5$, in acetone), fell from an initial −14·5° to a final −4·7°. This result, and some similar ones obtained with singly-labelled runs which were followed over long periods (weeks), are collected in Table 1.

TABLE 1. *Initial and final rotations* ($[\alpha]_D^{20}$, $c = 5$, *in acetone*) *of s-butylmercuric bromide, and exchange rates* ($k_0^{Alk.}$ *in mole* $l.^{-1}$ $sec.^{-1}$), *in polarimetrically followed exchanges with di-s-butylmercury in ethanol at* 35·0°.

No.	[Bu^sHgBr] = [Bu^s_2Hg]	[LiBr]	Rotations Initial	Rotations Final	No. of ½-lives followed	$10^7 k_0$Alk
1	0·1	—	−14·5°	−4·7°	14	4·6
3	0·1	—	−12·15	−3·95	19	4·7
4	0·1	—	−12·2	−4·0	~20	4·8
7*	0·1	0·1	−10·2	−3·25	28	10·1

* It is shown in a separate experiment that lithium bromide, although it accelerates the exchange and therefore the fall of rotation, does not cause racemisation of s-butylmercuric bromide in the absence of s-dibutylmercury, in otherwise the same conditions.

All this proves that the three-alkyl substitution proceeds with total retention of configuration. If it were accompanied by partial or complete racemisation, the rotation of the s-butylmercuric bromide would fall to zero. If it proceeded with configurational inversion, even total inversion, the rotation would still fall to zero.

(4) *Kinetics of the Three-alkyl Substitution.*—Our first concern was to confirm the identification (Section 2) of the reaction of s-butylmercuric bromide with di-s-butylmercury as a three-alkyl electrophilic substitution (3); and, as to this, we did two things. The first was to generalise the double-labelling method. For the principle, by which the exchange reaction may be identified according to whether the ratio, mercury-exchange/alkyl-exchange, is unity, one-half, or zero, can obviously be applied, not only, as we did it originally, by simultaneous double-labelling, but also by putting the alternative labels into parallel experiments. Our comparison of exchange rates with this generalisation of method is set out in Table 2. One sees that the rate of exchange, whether of mercury measured by radioactivity, or of alkyl followed by optical activity, is the same; and that therefore, by this test, the process is indeed the substitution (3).

In our radiometric measurements generally, we sometimes put the radiomercury (^{203}Hg) originally into the s-butylmercuric bromide, and sometimes into the di-s-butylmercury, the latter substance being made from the former by the Grignard method. In the experiments of Table 2, the radioactivity was originally in the s-butylmercuric bromide.

TABLE 2. *Rates of exchange of alkyl and mercury (k_0^{Alk} and k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$) between s-butylmercuric bromide* (0·1M) *and di-s-butylmercury* (0·1M) *in ethanol at* 35·0°.

By optical activity			By radioactivity		
Run	$10^7 k_0^{Alk}$	Mean	Run	$10^7 k_0^{Hg}$	Mean
1	4·6		1	4·4	
3	4·7	4·7	54	4·9	4·6
4	4·8		57	4·4	

A second kinetic method has been applied to the distinction between the three-alkyl substitution (3) and its simulation by two steps of the known two-alkyl substitution (2). The principle is as follows. A zeroth-order rate of exchange will usually depend on the concentrations of the exchanging species. The nature of the dependence will not necessarily be indicated by the kinetic forms of the observed label-transfers, because these will be of first order whatever the mechanism of exchange, if no reactions other than exchange are going on. However, the form of the dependence can be found by varying the concentrations of the reactants, which are, of course, constants of the individual experiments. If, independently of the degree of labelling, a is the concentration of s-butylmercuric bromide, and b is that of the di-s-butylmercury, and if k_0 is the rate of exchange as measured by the rate of transfer of either of our labels, then, supposing that exchange proceeds in a single step, as of substitution (3) exemplified by equation (4), we should find that a second-order rate-constant, defined by the equation $k_2^{(3)} = k_0/ab$, would be invariant with changing a and b, apart from medium effects. However, if exchange occurs through two successive steps of substitution (2), *i.e.*, two reversible processes of label-transfer, as illustrated in equations (6), then one can show that another second-order rate-constant of substitution, $k_2^{(2)} = k_0/a^2$, should be invariant with changing a and b, except for medium effects. As is shown in the Appendix (p. 1132), these relations hold, according to mechanism, without making any difference to the form of the time-dependent observations from which the label-transfer rate-constant k_1, and thence the exchange rate k_0, are derived, as explained in Section 2.

A determination of the dependence of k_0 on a and b constitutes, not only a confirmatory test of our identification of the chemical nature of the substitution, but also a first essential contribution to the kinetic elucidation of its mechanism. For it is a test of whether the reaction goes in one step or more than one. If it goes in one step, then it must be the three-alkyl substitution, with a mechanism of molecularity two. However, the three-alkyl substitution could conceivably occur by way of a slow ionisation of the dialkylmercury, *i.e.*, by a mechanism of molecularity one. Actually our optical result (Section 3), that configuration is completely retained in the substitution, goes far to exclude this interpretation; but if it were true, the kinetic consequence would be that, medium effects apart, yet another rate-constant of substitution, a first-order one, $k_1^{(3)} = k_0/b$, would be invariant with changing a and b, again without alteration to the form of the time-dependent observations.

The results of these measurements, made with mercury-labelling, are in Table 3. They confirm that the reaction is not a composition of steps of the two-alkyl substitution, but is a three-alkyl substitution, which, moreover, proceeds in one bimolecular step. The rate of exchange, k_0^{Hg}, obviously varies systematically with the concentrations of both reactants. The rate-constants of substitution, $k_2^{(2)}$ and $k_1^{(3)}$, also vary with the concentration of at least one of the reactants. The substitution rate-constant, $k_2^{(3)}$, is, however, relatively steady. Most of the variation in its individual values can be assigned to

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experimental error, though the apparent small rise with the concentration of s-butylmercuric bromide may well be genuine, and, if so, may be a medium effect: we demonstrate below the kinetic effect of certain added lithium salts.

Salt effects on this reaction were examined in order to provide further evidence of mechanism. The effect of added lithium salts on the second-order rate-constant of substitution, $k_2^{(3)}$, is generally one of acceleration. In the case of lithium acetate the

TABLE 3. *Radiometrically measured rates of mercury exchange (k_0^{Hg}, in mole l.$^{-1}$ sec.$^{-1}$) and first-order ($k_1^{(3)}$ in sec.$^{-1}$) and second-order ($k_2^{(2)}$ and $k_2^{(3)}$ in mole^{-1} l. sec.$^{-1}$) rate-constants of substitution by s-butylmercuric bromide (concentration a) in di-s-butylmercury (concentration b) in ethanol at 35·0°.*

Run	*a* (M)	*b* (M)	$10^7 k_0^{Hg}$	$10^5 k_2^{(2)}$	$10^6 k_1^{(3)}$	$10^5 k_2^{(3)}$
1	0·1	0·1	4·4	4·4	4·4	4·4
54	0·1	0·1	4·9	4·9	4·9	4·9
57	0·1	0·1	4·4	4·4	4·4	4·4
49	0·12	0·1	6·0	4·2	6·0	5·0
50	0·14	0·1	7·5	3·8	7·5	5·4
78 *	0·1	0·06	2·4	2·4	4·0	4·0
46	0·1	0·15	7·9	7·9	5·3	5·3
51	0·1	0·18	7·8	7·8	4·3	4·3

* In this experiment, the radiomercury was initially in the di-s-butylmercury; in all others of this Table, it was initially in the s-butylmercuric bromide.

effect was very small indeed, not quite clearly outside the experimental error. Lithium nitrate produced a somewhat small, but definitely demonstrable effect, lithium bromide a larger one, and lithium perchlorate a somewhat larger one still. All these accelerating effects are trifling compared to some we shall have to consider in Part V (accompanying). In the example of lithium bromide, we examined the form of the dependence of the rate-increase on the concentration of the added salt: the logarithm of the rate increased with a power of the concentration, which was less than one, but more than one-half. Some of these measurements were made radiometrically, by way of the rate of mercury exchange k_0^{Hg}, and others polarimetrically, through the rate of alkyl exchange $k_0^{Alk.}$. The results are in Table 4. They are discussed in Section 5.

TABLE 4. *Effects of added lithium salts on the second-order rate-constants of substitution ($k_2^{(3)}$ in mole^{-1} l. sec.$^{-1}$) by s-butylmercuric bromide (0·1M) in di-s-butylmercury (0·1M) in ethanol at 35·0°.*

Run	[Salt]	$10^5 k_2^{(3)}$	Mean	Run	[Salt]	$10^5 k_2^{(3)}$	Mean
Lithium acetate (radiometric)				*Lithium bromide (polarimetric)*			
1, 54, 57	0·0	4·4—4·9	4·6	1, 3, 4	0·0	4·6—4·8	4·7
55	0·1	5·6		12	0·025	6·2	6·2
56	0·1	5·5		8	0·05	7·7	7·9
58	0·1	4·8	5·0	7	0·1	10·1	10·0
69 *	0·1	4·7		10	0·1	10·0	
73 *	0·1	4·6		9	0·125	11·2	11·2
				11	0·2	14·8	14·8
Lithium nitrate (radiometric)				*Lithium perchlorate (polarimetric)*			
1, 54, 57	0·0	4·4—4·9	4·6	1, 3, 4	0·0	4·6—4·8	4·7
70 *	0·1	5·9		22	0·1	11·7	
71 *	0·1	6·1	6·0	23	0·1	12·4	12·0
72 *	0·1	6·1		24	0·1	11·8	
76 *	0·15	7·5	7·5	25	0·1	11·9	

* In these experiments, the radiomercury was initially in the di-s-butylmercury; in all others on the left-hand side of this Table, it was initially on the s-butylmercuric bromide.

In the work of Part II on the two-alkyl mercury exchange,[1] useful evidence of the mechanism of the second-order reaction between mercuric salts and di-s-butylmercury was obtained by changing the anions of the salts: it was a significant result that substitution-rate increased along the anion series, bromide, acetate, nitrate, without disturbance

to the kinetic form of substitution. Therefore our next proceeding was to investigate the kinetic effect of changing the anion of our s-butylmercuric substituting agent, from bromide, to acetate, and then to nitrate.

The three-alkyl substitution by s-butylmercuric acetate went considerably faster than by s-butylmercuric bromide. The reaction of the acetate was followed radiometrically in ethanol at 35°, with the radiomercury initially in the di-s-butylmercury:

$$BuHg{\cdot}OAc + Bu_2{}^{*}Hg \rightleftharpoons Bu_2Hg + Bu{}^{*}Hg{\cdot}OAc$$

The results are in Table 5. From the observed rate of mercury exchange, k_0^{Hg}, we calculated the second-order rate-constant for the three-alkyl substitution, $k_2^{(3)}$. We did not prove directly that this is the correct rate-constant of substitution to calculate, but such proof is given, both (above) for the slower substitution of s-butylmercuric bromide, and (below) for the faster one of s-butylmercuric nitrate, wherefore it cannot be doubted that the same kinetics prevail throughout the series.

TABLE 5. *Radiometrically measured rates of mercury exchange (k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$) between s-butylmercuric acetate and radiomercury-containing di-s-butylmercury and second-order rate-constants of substitution ($k_2^{(3)}$ in mole^{-1} l. sec.$^{-1}$) in ethanol at 35·0°.*

Run	[BuHg·OAc] = [Bu_2Hg]	$10^6k_0^{Hg}$	$10^4k_2^{(3)}$	Mean
80	0·1	2·9	2·9	2·7
81	0·1	2·7	2·7	
82	0·1	2·6	2·6	

The substitution by s-butylmercuric nitrate in di-s-butylmercury is much faster than either of the substitutions described above. The reaction of the nitrate was followed, like that of the acetate, by radiometric measurement of the rate of mercury exchange, the radiomercury being initially in the di-s-butylmercury:

$$BuHg{\cdot}NO_3 + Bu_2{}^{*}Hg \rightleftharpoons Bu_2Hg + Bu{}^{*}Hg{\cdot}NO_3$$

The solvent was again ethanol, but, because of the high rates, the temperature was reduced to 0°, and even then the measurable exchange was over within a few minutes.

In this study, we varied the concentrations of the reactants independently, and, from the observed rates of mercury exchange, k_0^{Hg}, we calculated the various possible rate-constants of substitution, *viz.*, the second-order constant, $k_2^{(2)}$, corresponding to a pair of steps of the two-alkyl process (2), and the first- and second-order constants, $k_1^{(3)}$ and $k_2^{(3)}$, representing different mechanisms of the three-alkyl substitution (3). The results, which are in Table 6, clearly exclude two-alkyl substitution and the first-order mechanism of three-alkyl substitution: the rate-constants representing these processes obviously vary systematically with one or both reactant concentrations. The only rate-constant of which the scatter is restricted to the order of magnitude of the observational uncertainty is the second-order three-alkyl constant $k_2^{(3)}$. Thus it is proved for the reaction of s-butylmercuric nitrate, as it has been for that of s-butylmercuric bromide, that the mechanism of substitution involves a single second-order step of the three-alkyl process (3).

Table 6 contains a suggestion that the second-order three-alkyl constant, $k_2^{(3)}$, increases a little with increasing concentration of s-butylmercuric nitrate. The effect seems somewhat larger than the experimental error. It may be a salt effect analogous to that, next to be scribed, of added lithium nitrate.

Our examination of salt effects on the reaction of s-butylmercuric nitrate was necessarily confined to salts which do not exchange their anion with the substituting agent to give a different one. Of the four salts used previously, only lithium nitrate and perchlorate were suitable for the present study: in fact, we used lithium nitrate. The addition of this salt mildly accelerated the substitution, as followed by mercury exchange, by s-butylmercuric nitrate. As shown in Table 7, the lithium salt, in concentration 0·15M, increased

the second-order three-alkyl rate-constant, $k_2^{(3)}$, by about 1·5 times. This is nearly the same as the factor by which, as seen in Table 4, the same concentration of the same salt increases the rate of substitution by s-butylmercuric bromide in di-s-butylmercury. The significance of this and other salt effects is considered in Section 5.

TABLE 6. *Radiometrically measured rates of mercury exchange (k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$) and first-order ($k_1^{(3)}$ in sec.$^{-1}$) and second-order ($k_2^{(2)}$ and $k_2^{(3)}$ in mole^{-1} l. sec.$^{-1}$) rate-constants of substitution by s-butylmercuric nitrate (concentration a) in radiomercury-containing di-s-butylmercury (concentration b) in ethanol at 0·0°.*

Run	*a* (M)	*b* (M)	$10^4k_0^{Hg}$	$10^2k_2^{(2)}$	$10^3\,k_1^{(3)}$	$10^2k_2^{(3)}$	Mean
67	0·04	0·1	1·1	6·9	1·1	2·8	2·8
68	0·04	0·1	1·1	6·9	1·1	2·8	
44	0·06	0·1	1·7	4·7	1·7	2·8	2·9
48	0·06	0·1	1·8	5·0	1·8	3·0	
60	0·08	0·1	2·5	3·9	2·5	3·1	3·4
66	0·08	0·1	3·0	4·7	3·0	3·7	
35	0·1	0·1	3·5	3·5	3·5	3·5	3·4
39	0·1	0·1	3·4	3·4	3·4	3·4	
41	0·1	0·1	3·3	3·3	3·3	3·3	
65	0·13	0·1	4·7	2·8	4·7	3·6	3·6
45	0·1	0·03	1·1	1·1	3·7	3·7	3·6
74	0·1	0·03	1·05	1·05	3·5	3·5	
64	0·1	0·14	4·3	4·3	3·1	3·1	3·0
75	0·1	0·14	4·0	4·0	2·9	2·9	

TABLE 7. *Effect of lithium nitrate on the radiometrically measured rate of mercury exchange (k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$), and on the second-order rate-constant of substitution ($k_2^{(3)}$ in mole^{-1} l. sec.$^{-1}$) by s-butylmercuric nitrate (concentration a) in radiomercury-containing di-s-butylmercury (concentration b) in ethanol at 0·0°.*

Runs	*a* (M)	*b* (M)	[$LiNO_3$]	$10^4k_0^{Hg}$	$10^2k_2^{(3)}$	Mean
All Tab. 6	Various	Various	0·0	Various	2·8—3·7	3·25
35, 39, 41	0·1	0·1	0·0	3·3—3·5	3·3—3·5	3·4
36	0·1	0·1	0·15	5·2	5·2	4·9
40	0·1	0·1	0·15	4·6	4·6	
42	0·1	0·1	0·15	4·8	4·8	

(5) *Mechanism of the Substitution.*—The reaction here considered has been identified as exemplifying the three-alkyl substitution (3), by double-labelling, and confirmatorily by kinetics, methods which exclude all other possible interpretations of the overall stoicheiometry. Three-alkyl substitution is a new reaction: the question of its mechanism therefore arises; and we shall consider the three electrophilic mechanisms of substitution, unimolecular S_E1, bimolecular S_E2, and internal S_Ei, preconceived in Part I.[2]

The complete retention of configuration in the substitution, and its second-order kinetic form, agree in excluding mechanism S_E1. But both results are consistent with either mechanism S_E2 or S_Ei. The rest of our kinetic investigation was designed to resolve this ambiguity; and again we can offer two separate pieces of evidence.

The question is essentially one of deciding whether an open or a cyclic formula best expresses the transition state of substitution, apart from its solvation. Our first method of attacking this problem is the same as one used in connexion with the two-alkyl substitution treated in Part II,[1] *viz.*, to examine the effect on rate of increasing the ionicity of the substituting agent, or, what comes to the same, making its potential or actual anion successively less prone to combine with the mercury atom which is being expelled. We find that the rate of substitution increases along the reagent-series, $Bu^sHgBr < Bu^sHg{\cdot}OAc \ll Bu^sHg{\cdot}NO_3$, where the single inequality sign expresses one power of ten,

and the double one at least two powers. Such an increase of rate with ionicity is clearly more consistent with mechanism S_E2 than with mechanism S_Ei.

To provide confirmatory evidence, we studied kinetic salt effects on the substitutions using the extreme members of our reagent series, s-butylmercuric bromide and s-butylmercuric nitrate. It is useful to recall what happened in the similar study, in Part II,[1] of the two-alkyl reaction: the striking result was a strong specific retardation by lithium bromide of the reaction of mercuric bromide with di-s-butylmercury, according to a kinetic form which showed clearly that bromide ion was combining fairly firmly with mercuric bromide to form the complex anion, $HgBr_3^-$, the mercury atom in which was practically put out of action as an electrophilic substituting agent in this reaction. In the present study of salt effects on the three-alkyl reactions, the general result was that lithium salts weakly or moderately accelerate them, and that lithium bromide, in its effect on the reaction of s-butylmercuric bromide with di-s-butylmercury, is no exception. This shows, first, that bromide ion does not combine with alkylmercuric bromides to form complex anions $RHgBr_2^-$ nearly as firmly as it combines with mercuric bromide to form $HgBr_3^-$. We may also conclude from the general result that the transition states of the three-alkyl substitutions are more polar than their initial states; and that this is as true when the reagent is s-butylmercuric bromide as when it is s-butylmercuric nitrate; for the accelerating effects of the same salt in these two reactions were practically identical.

The accelerating effect of different lithium salts on the same reaction, that of s-butylmercuric bromide, followed broadly the tendency to ionic dissociation of the lithium salts. The order of the accelerating effects was: $LiOAc < LiNO_3 < LiBr < LiClO_4$, with only a small difference between the last two members of this series. We must remember in this connexion that a bromide, although among the least ionised of mercuric salts, and in this regard very different from the perchlorate,* is among the most ionically dissociated of lithium salts, and in this respect is comparable to the perchlorate. Indeed, as we know that, at least in acetone at greater dilutions than we here use, lithium bromide is more fully dissociated than the perchlorate,[9] we might have expected lithium bromide, if distinguishable from the perchlorate in its salt effect, to stand on the other side of it in our salt series. We would hesitate to speculate on the cause of this minor anomaly were there not further reason in the following papers for our interpretation, which is that bromide ion does have an appreciable affinity for alkylmercuric bromides, though not nearly so strong a one as for mercuric bromide; and that its association with s-butylmercuric bromide lowers the activity of that substance as an electrophilic reagent. In other words, we suggest that lithium bromide, in addition to its accelerating general salt effect, has a more weakly retarding specific effect on the three-alkyl substitution. The balance is the opposite of that obtaining in the two-alkyl substitution: there, the general effect of lithium bromide cannot be seen, because its specific effect is so powerful.

The above is only the fitting of a detail into the broad picture of the salt effects. This discloses a transition state of three-alkyl substitution, which is of similar form throughout the series of reactions studied, is a highly polar transition state, and is therefore probably an open one, apart from solvation, consistently with mechanism S_E2.

In the light of all our optical and kinetic evidence, our conclusion, in summary, is that, in the reactions of s-butylmercuric bromide, acetate, and nitrate, severally, with di-s-butylmercury in ethanol, the mercury-for-mercury replacement is a three-alkyl substitution, having the bimolecular electrophilic mechanism, S_E2, in which stereochemical

* Presumably the unshared valency electrons of iodine ($5p$), bromine ($4p$), and, though more mildly, chlorine ($3p$), in mercuric salts, can conjugate effectively with the empty orbitals ($6p$) of the valency shell of mercury ($+T$-effect), whereas those of fluorine ($2p$), as of oxy-anions ($2p$), are too close to their nuclei to do so (and in oxy-anions are otherwise delocalised). However, orbital size-adjustment must be an important factor in the conjugation of the higher halogens.

[9] Dippy, Jenkins, and Page, *J.*, 1939, 1386; Evans and Sugden, *J.*, 1949, 270; Accascina and Schiavo, *Ann. Chim.* (*Italy*), 1953, **43**, 695; A. J. Parker, personal communication.

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configuration is fully preserved. Thus, the three-alkyl substitution appears to be closely analogous in mechanism to the two-alkyl substitution,† on which we reported in Part II.[1]

Experimental

(6a) *Materials.*—Most of the racemic or optically active s-butylmercuric salts, and the di-s-butylmercury, required for this work were prepared as described in Parts I and II,[2,1] and the following notes are supplementary. The preparation of s-butylmercuric nitrate was greatly improved by adding the nitric acid to the s-butylmercuric hydroxide under cooling with ice–salt, the internal temperature being close to 0°, and crystallising the initially obtained pink solid from ether–pentane between 20° and −80°; a good yield of colourless crystals, m. p. 51°, was obtained. *s-Butylmercuric acetate*, not described before, was prepared by reaction of di-s-butylmercury (10 g.) with mercuric acetate (10 g.) in methanol (100 ml.). After being kept overnight, the solution was filtered and evaporated under reduced pressure, the oily residue was taken up in ether, and the filtered extract was evaporated at room temperature. The solid residue was crystallised three times from pentane between 20° and −80°, whereupon its m. p. 29° became constant (Found: C, 22·4; H, 3·7. $C_6H_{12}HgO_2$ requires C, 22·7; H, 3·8%). Radioactive materials were prepared, starting from pile-irradiated mercuric oxide, after the short-lived isotopes (half-lives of the order of a day or less) had disappeared, and only ^{203}Hg (half-life 46·5 days) and stable isotopes remained. This material, after dilution with inactive mercuric oxide, was converted by hydrobromic acid into radiomercuric bromide, which, after further dilution with mercuric bromide, was crystallised from ethanol. The product, on reaction with di-s-butylmercury, under conditions given by the kinetic investigation of Part II, produced s-butylradiomercuric bromide. Some of this product was converted by the Grignard method (cf. Part II) into di-s-butylradiomercury. Optically active s-butylradiomercuric bromide was made by the reaction of radiomercuric bromide, in the presence of lithium bromide, with optically active di-s-butylmercury (Part II), under conditions given by the kinetic investigation of Part V (accompanying). All these organic mercury compounds were stored in the dark at −80°.

(6b) *Polarimetric Kinetics with s-Butylmercuric Bromide.*—The optically active s-butylmercuric bromide was crystallised from pentane, and the racemic di-s-butylmercury was distilled under reduced pressure, just before use. The ethanol was dried by the method employing ethyl phthalate. After its optical rotation had been checked, weighed s-butylmercuric bromide was dissolved in most of the required ethanol at 35°, weighed di-s-butylmercury was added, and the volume was adjusted. Initially, and after known times at 35·0°, samples of 25 ml. were withdrawn, each to be run into an empty tube immersed in solid carbon dioxide–acetone. The precipitated s-butylmercuric bromide was collected and washed with pentane, and its specific rotation ($c = 5$, in acetone) was determined. Runs in which lithium salts were initially added were sampled in the same way, except that the recovered s-butylmercuric bromide was washed with water, and, when dry, with pentane. These procedures were shown to be correct by the check that the specific rotation of s-butylmercuric bromide thus recovered from the initially withdrawn sample was identical with that of the material used to make up the reaction solution. Rates of exchange, and rate-constants of substitution, determined in this way, are in Tables 1, 2, and 4. The course of an individual run is shown in Table 8.

(6c) *Radiometric Kinetics with s-Butylmercuric Bromide.*—In some runs s-butylradiomercuric bromide was used with non-radioactive di-s-butylmercury, and in others inactive

† Dessy and Lee [10] have recently proposed a mechanism of S_Ei-type for the two-alkyl substitution, on the basis of their study of the rates of reaction of mercuric iodide with several dialkyl- and diarylmercurys in dry or aqueous dioxan. They embrace both the aliphatic and aromatic electrophilic substitutions in a single mechanism, though π-electrons might be expected to play a rôle in the aromatic substitutions. Their sharpest, indeed, their only sharp piece of evidence rests on their statement, unsupported by comparative figures, that the rate of reaction of mercuric iodide with diphenylmercury is unaffected by added lithium iodide. Since we know from the work of our Part II [1] that the reaction of mercuric bromide with di-s-butylmercury is strongly retarded by lithium bromide, their observation, if confirmed, would argue against a common aliphatic-cum-aromatic mechanism. However, the measurements were by light-absorption of mercuric iodide, and the experiment with added lithium iodide is not detailed, though these two salts would be expected to combine enough to change the absorption spectrum.

[10] Dessy and Lee, *J. Amer. Chem. Soc.*, 1960, **89**, 689.

s-butylmercuric bromide with di-s-butylradiomercury. In either case, s-butylradiomercuric bromide was isolated from timed samples of 25 ml. according to the procedure of Section 6b. The radiation counts were taken on 10 ml. of a solution of this substance in acetone in concentrations (not above 0·1M) and over periods (not above 1 hr.) adjusted according to the activity. Counts were corrected for background, and allowance was made for the slow decay of ^{203}Hg by re-counting the initial sample on the day of the counting of any timed sample. Rates of exchange, and rate-constants of substitution, measured thus, are in Tables 2, 3, and 4. The course of an individual run is shown in Table 9.

(6d) *Radiometric Kinetics with s-Butylmercuric Acetate.*—These runs were followed by using non-radioactive s-butylmercuric acetate and di-s-butylradiomercury in ethanol at 35·0°.

TABLE 8. (*Run* 3) *Polarimetric rate of exchange* (k_0^{Alk} *in mole* $l.^{-1}$ $sec.^{-1}$) *and second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *of optically active s-butylmercuric bromide and racemic di-s-butylmercury in ethanol at* 35·0°.

([Bu^sHgBr] = 0·1M; [Bu^s_2Hg] = 0·1M; $[\alpha]_D^{20}$ for $c = 5$, in acetone; $f = (3[\alpha_t] - [\alpha_0])/2[\alpha_0]$; $k_1 = -(1/t) \ln f$; $k_0^{Alk} = 0{\cdot}2k_1/3$; $k_2^{(3)} = 100k_0^{Alk}$).

t (hr.)	0·0	19·0	24·0	29·0	43·0	49·0	69·5	116·5	504
$[\alpha_t]_D^{20}$	−12·15°	−8·93	−8·57	−7·98	−6·76	−6·41	−5·23	−4·42	−3·95
100 $(1 - f)$	0·0	39·8	44·2	51·6	66·6	70·9	85·6	95·5	101
10^6k_1 ($sec.^{-1}$)	—	7·41	6·74	6·96	7·06	6·99	7·72	7·17	—
$10^7k_0^{Alk} = 10^5k_2^{(3)}$	—	4·94	4·49	4·62	4·71	4·66	5·15	4·78	—

TABLE 9. (*Run* 55) *Radiometric rates of exchange* (k_0^{Hg} *in mole* $l.^{-1}$ $sec.^{-1}$) *and second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *of s-butylradiomercuric bromide with inactive di-s-butylmercury in the presence of lithium acetate in ethanol at* 35·0°.

([Bu^sHgBr] = 0·1, [Bu^s_2Hg] = 0·1, [LiOAc] = 0·1M; corrected count, c; $f = (2c_t - c_0)/c_0$; $k_1 = -(1/t) \ln f$; $k_0^{Hg} = 0{\cdot}1k_1/2$; $k_2^{(3)} = 100k_0^{Hg}$.)

t (hr.)	c_t	100 $(1 - f)$	10^6k_1 ($sec.^{-1}$)	$10^7k_0^{Hg} = 10^5k_2^{(3)}$
0·0	7674	0·0	—	—
14·0	6028	44·6	11·7	5·8
18·0	5741	52·1	11·4	5·7
22·0	5483	58·8	11·2	5·6
26·0	5162	67·2	11·9	5·8
39·0	4727	78·2	10·9	5·4

Timed samples of 25 ml. were run into empty tubes immersed in solid carbon dioxide–acetone, and, to each, 10 ml. of 10% aqueous potassium bromide were added to precipitate s-butylradiomercuric bromide, which was collected and washed with water and, when dry, with pentane. Its radioactivity was measured as described in Section 6c. The rate-constants are in Table 5, and a specimen run is recorded in Table 10.

TABLE 10. (*Run* 81) *Radiometric rate of exchange* (k_0^{Hg} *in mole* $l.^{-1}$ $sec.^{-1}$) *and second-order rate-constants of substitution* ($k_2^{(3)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *of s-butylmercuric acetate with di-s-butylradiomercury in ethanol at* 35·0°.

([$Bu^sHg{\cdot}OAc$] = 0·1M; [Bu^s_2Hg] = 0·1M; formulæ as in Table 9, except that $f = (c_\infty - c_t)/c_\infty$ with c_∞ = half the count of initially used Bu^s_2Hg.)

t (hr.)	c_t	100 $(1 - f)$	10^6k_1 ($sec.^{-1}$)	$10^7k_0 = 10^5k_2^{(3)}$
1·0	1583	18·1	55·5	27·7
2·5	3382	38·8	54·5	27·2
4·0	4564	52·2	51·4	25·7
6·0	5980	68·5	53·5	26·8
∞	8740	100	—	—

(6e) *Radiometric Kinetics with s-Butylmercuric Nitrate.*—The exchange between non-radioactive s-butylmercuric nitrate and di-s-butylradiomercury was too fast to measure at 35°, but was followed at 0° with the aid of a rapid-sampling technique. At a known time, about 25 ml. (not measured) of the solution were poured directly from the reaction flask into an empty tube cooled in liquid nitrogen. This quenching procedure was tested and shown to be adequate. Samples were thus quenched every 20—40 sec., depending on the rate, over periods between

1 and 4 min. They rapidly solidified and were afterwards placed for some hours in a bath of solid carbon dioxide–acetone, where they re-melted and deposited crystalline s-butylmercuric nitrate. The mother-liquor was decanted from each such sample of this salt, to which, after it had been washed with cooled ethanol by decantation, a few ml. of dioxan, then a calculated excess of 60% aqueous hydrobromic acid, and then water, were added. The s-butylradiomercuric bromide, which crystallised, was collected, and its radioactivity was measured as described in sections 6d and 6c. The rate-constants, calculated from four-point runs, such as that in Table 10, and by the same formulæ, are in Tables 6 and 7.

Appendix

(7) *Rate Equations.*—First consider the chemical equation (4) (p. 1122) as if written reversibly. If a and b are the concentrations of alkylmercuric salt and dialkylmercury, respectively, and x is the concentration of labelled mercury, originally in one of them, which has become transferred to the other at time t, then, because the rate-constant for bimolecular three-alkyl substitution $k_2^{(3)}$ must be the same for both directions, the rate of label-transfer will be

$$dx/dt = k_2^{(3)}\{(a - x)(b - x) - x^2\} = k_2^{(3)}\{ab - (a + b)x\} \quad . \quad . \quad . \quad . \quad (i)$$

At infinite time, $dx/dt = 0$, and hence $x_\infty = ab/(a + b)$. At zero time, $x = 0$, and hence

$$k_0^{Hg} = (dx/dt)_0 = k_2^{(3)}ab \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

where $k_2^{(3)}$ is to be calculated from the integrated form of (i), which is

$$k_2^{(3)} = k_1/(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

$$k_1 = -(1/t) \ln f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv)$$

$$f = (x_\infty - x)/x_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (v)$$

Now consider the chemical equations (6) (p. 1123) as if written reversibly. Let $k_2^{(2)}$ be the rate-constant of formation of mercuric bromide by bimolecular two-alkyl substitution, and $k_2^{(-2)}$ the much larger rate-constant for the reverse of this reaction. An unlabelled molecule of mercuric bromide can be formed either from two unlabelled molecules of the alkylmercuric bromide, or from one labelled and one unlabelled; and a labelled mercuric bromide molecule can be formed either from the latter combination or from two labelled molecules. The mercuric bromide molecule produced in each of these four ways can react with either labelled or unlabelled dialkylmercury, to produce, in the one case, a pair of molecules like those it came from, and, in the other, an alternative pair containing a transferred label. Thus of the eight reaction sequences which form and destroy mercuric bromide, four lead to label-transfer. Consider one of these four. Two unlabelled alkylmercuric bromide molecules will produce unlabelled mercuric bromide at a rate $k_2^{(2)}(a - x)^2$, and a fraction $(b - x)/b$ of this product will react with the labelled dialkylmercury to give label-transfer at a rate $k_2^{(2)}(a - x)^2(b - x)/b$. Adding in the other three contributions to the rate of transfer, taking due account of direction, we find

$$\begin{aligned} dx/dt &= (k_2^{(2)}/b)\{(a - x)^2(b - x) + (a - x)(b - x)x - (a - x)x^2 - x^3\} \\ &= k_2^{(2)}(a/b)\{ab - (a + b)x\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (vi) \end{aligned}$$

At zero time, $x = 0$, and hence

$$k_0^{Hg} = (dx/dt)_0 = k_2^{(2)}a^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (vii)$$

where $k_2^{(2)}$ is to be calculated from the integrated form of (vi). This is

$$k_2^{(2)} = k_1 b/a(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (viii)$$

where k_1 is given by equations (iv) and (v).

From either (ii) and (iv), or (vii) and (iv),

$$k_0^{Hg} = k_1 ab/(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ix)$$

Hence k_0 can be determined without assumptions as to which mechanism is responsible for exchange, and then the validity of the mechanism-dependent equations (ii) and (vii) can be tested, as in Section 4. This analysis is given for a mercury label. It is the same for an alkyl

label, except that various factors of 2 and ½ enter into the working, which compensate. A similar derivation can be given of the relations between the unimolecular substitution constant $k_1^{(3)}$, and the exchange and label-transfer constants, k_0^{Hg} and k_1. All these relations are used in Sections 4 and 6.

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[*Received, September 20th*, 1960.]

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227. *Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part IV.* Kinetics, Stereochemistry, and Mechanism of the Uncatalysed One-alkyl Mercury-exchange Reaction.*

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The reactions of mercury exchange of methylmercuric and/or s-butylmercuric bromide, iodide, acetate, and nitrate, with mercuric salts having corresponding anions, exemplify the formerly expected, but now newly recognised, one-alkyl form of electrophilic mercury-for-mercury substitution, which here proceeds in ethanol by mechanism S_E2 with full retention of configuration. The evidence is as follows. It is shown by a radiometric study of the kinetics of the mercury exchanges, that they go in a single bimolecular step. By using optically active s-butylmercuric acetate, it is shown in a correlated polarimetric study that the substitution produces no loss of optical activity. By increasing the ionicity of the salts along the anion-series mentioned, and noting the associated large increase in rate, it is shown that reaction is not assisted by combination between the anion of the substituting agent and the mercury atom being expelled, *i.e.*, that we have an open, rather than a closed, transition state. Confirmatively, substantial positive salt-effects and polar co-solvent-effects are observed, which show that the transition states are considerably more polar than the initial states.

All the three expected forms of aliphatic mercury exchange have now been observed and their mechanisms demonstrated.

(1) *Previous Work.*—The one-alkyl electrophilic mercury-for-mercury substitution can be demonstrated only with the aid of isotopically labelled mercury, as by radioactive ^{203}Hg, in an isotopic exchange reaction, such as the following, where the asterisk signifies the label:

$$Me{\cdot}HgBr + {}^{*}HgBr_2 \rightleftharpoons Me{\cdot}{}^{*}HgBr + HgBr_2$$

This isotopic exchange was first described by Nefedov and Sintova.[1,2] They did not recognise it as a new form of substitution. Reutov generalised it to other alkyl groups including cycloalkyl and arylalkyl groups.[3,4,5] He recognised it as depending on electrophilic substitution. With Knoll and Wu Yan-Tsei, he studied its stereochemistry, both with geometrical isomers in the cyclohexane series and with menthyl derivatives having centres of asymmetry, besides the metal-bearing one, in optically active form.[3] These authors concluded that configuration is retained.

Nefedov and Sintova regarded their reaction, not as the individual process formulated

* Part III, preceding paper.

[1] Nefedov and Sintova, "Collected Works on Radiochemistry," Leningrad University Press, 1955, p. 113.
[2] Nefedov, Sintova, and Frolov, *Zhur. fiz. Khim.*, 1956, **30**, 2356.
[3] Reutov, Knoll, and Wu Yan-Tsei, *Doklady Akad. Nauk S.S.S.R.*, 1958, **120**, 1052.
[4] Reutov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1958, 684.
[5] Reutov, *Angew. Chem.*, 1960, **72**, 198.

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above, but as the overall result of two successive substitutions of the long-familiar two-alkyl type:

$$2MeHgBr \rightleftharpoons Me_2Hg + HgBr_2$$

$$Me_2Hg + {}^{*}HgBr_2 \rightleftharpoons {}^{*}MeHgBr + MeHgBr$$

Their reasons for this view are not apparent. Their rate figures, though neither extensive nor accurate enough to justify a positive conclusion, tend more against their interpretation than in favour of it. However, the interpretation seems to have been accepted, at least until recently, when Reutov remarked [5] that some unpublished work had convinced him that it could not be generally valid.*

(2) *Kinetic Form of the Uncatalysed One-alkyl Substitution.*—This history exposes the first essential question, *viz.*, that of whether the exchange is indeed the independent one-alkyl substitution, which was anticipated as a realisable electrophilic substitution in Part I [6] [cf. equations (*a*) and (1) of the preceding paper], when it would be, not observationally new, but a newly identified reaction, demanding an investigation of its mechanism, or whether it is a composition of steps of the well-known two-alkyl electrophilic substitution [cf. equations (*c*) and (2) of the preceding paper], in which case there would be nothing more to do, since the mechanism of that reaction for simple alkyl groups has been established (Part II [7]).

This question cannot be answered, like the similar one concerning three-alkyl substitution, dealt with in Part III,[8] by double-labelling; but it can by a suitable study of kinetic form. The formulæ of the Appendix of Part III [8] apply with little change. If a is the concentration of the substituting agent, here the mercuric salt, and b is that of the compound substituted, *viz.*, the alkylmercuric salt, then, independently of the mechanism of exchange, the observational first-order rate-constant of label-transfer, k_1^{Hg}, will give an exchange-rate, $k_0^{Hg} = k_1^{Hg}ab/(a + b)$. And then, if exchange depends on a succession of two-alkyl substitutions, a second-order constant $k_2^{(2)} = k_0^{Hg}/b^2$, will be invariant with changing a and b, apart from any medium effects. But if the exchange is manifesting a single one-alkyl substitution, then the only second-order constant which could possess this property is $k_2^{(1)} = k_0^{Hg}/ab$.

It will, however, possess it only if the one-alkyl substitution proceeds in a single step of molecularity two, as in either mechanism S_E2 or mechanism S_Ei (Part I [6]). But the single substitution might involve two distinct reactions, *e.g.*, a slow alkyl ionisation, followed by a rapid entry of the substituting agent, as in mechanism S_E1 (Part I [6]). In that case, no second-order constant will be invariant with changing a and b, but the first-order constant, $k_1^{(1)} = k_0^{Hg}/b$, will be so, apart from medium effects. Thus, if the one-alkyl substitution is indeed under observation, a determination of its kinetic form will not only identify it as such, but will also make a significant contribution to the establishment of its mechanism.

We first applied this procedure in Nefedov and Sintova's example,† that of mercury exchange between methylmercuric bromide and mercuric bromide in ethanol at 100°, with our label of the radioactivity of ^{203}Hg initially in the mercuric bromide. The rate-constants of label-transfer and exchange, and the various rate-constants of substitution, calculated therefrom according to mechanism, are in the uppermost portion of Table 1.

The constants $k_2^{(2)}$ and $k_1^{(1)}$ evidently vary systematically with the concentrations of one or both reactants, and only the constants $k_2^{(1)}$ exhibit no more scatter than is of the

* We made an equivalent statement in Part I,[6] on the basis of work preliminary to that now reported.

† These authors' exchange rates [2] are more than twice as large as ours in like conditions. We do not know the cause of the discrepancy, but it might arise from the circumstance that they separated methylmercuric bromide from mercuric bromide in timed reaction samples by steam-distilling the former, a method which, in our hands, led to exchange during separation.

[6] Charman, Hughes, and Ingold, *J.*, 1959, 2523.
[7] Charman, Hughes, and Ingold, *J.*, 1959, 2530.
[8] Charman, Hughes, Ingold, and Thorpe, preceding paper.

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order of the observational error. Any medium effects are within the range of casual variation of the rate constants. This result both identifies the exchange with one-alkyl substitution, and shows that this substitution proceeds in a single step.

The second portion of Table 1 shows the effect of temperature. We did not prove the applicability of the Arrhenius equation, but the substitution constants $k_2^{(1)}$ at 60° and 100° are given by the equation $k_2^{(1)} = 10^{7\cdot70} \exp(-19{,}800/\boldsymbol{R}T)$, which we shall use below for making an approximate extrapolation with respect to temperature.

The last section of Table 1 shows that the addition of 10% of water to the solvent ethanol accelerates the reaction by a factor of 1·83 at 100°. We take this to indicate that the reaction goes faster in more polar solvents generally, implying a polar transition state, for which we shall adduce further evidence below.

(3) *Kinetic Form: Generalisation to Other Anions, and to Another Alkyl Group.*—We report in this Section a series of analogous kinetic investigations, all with ethanol as

TABLE 1. *First-order rate-constants* (k_1^{Hg} *in sec.*$^{-1}$) *of transfer of radioactivity, rates of mercury exchange* (k_0^{Hg} *in mole l.*$^{-1}$ *sec.*$^{-1}$) *and first-order* ($k_1^{(1)}$ *in sec.*$^{-1}$) *and second-order* ($k_2^{(2)}$ *and* $k_2^{(1)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *rate-constants for substitution by mercuric bromide (concentration a) in methylmercuric bromide (concentration b).**

Run	*a* (M)	*b* (M)	$10^6k_1^{Hg}$	$10^7k_0^{Hg}$	$10^5k_2^{(2)}$	$10^6k_1^{(1)}$	$10^5k_2^{(1)}$
			In ethanol at 100·2°.				
14	0·100	0·100	25·6	12·8	12·8	12·8	12·8
50A	0·091	0·091	19·7	8·9	10·8	9·8	10·8
50B	0·163	0·100	35·0	21·7	21·7	21·7	13·3
30	0·181	0·091	35·9	21·6	26·2	23·8	13·2
13	0·091	0·181	34·8	21·0	6·4	11·6	12·8
29	0·272	0·050	44·7	18·9	75·6	37·8	13·9
19	0·290	0·096	49·4	35·6	38·7	37·1	12·8
129	0·091	0·190	34·3	21·1	5·8	11·1	12·2
57	0·091	0·243	37·1	24·5	4·2	10·1	11·1
121	0·100	0·272	49·5	36·2	4·9	13·3	13·3
122	0·254	0·226	61·4	73·5	14·4	32·5	12·8
128	0·391	0·231	86·5	126	23·5	54·4	13·9
123	0·378	0·281	84·4	136	17·2	48·4	12·8
						Mean:	12·8
			In ethanol at 59·8°.				
63	0·095	0·095	0·87	0·42	0·46	0·44	0·46
89	0·095	0·095	0·97	0·46	0·51	0·48	0·51
90	0·173	0·096	1·43	0·88	0·96	0·92	0·53
						Mean:	0·50
			In ethanol containing " 10% *" of water* † *at* 100·2°.				
130	0·091	0·091	43·6	19·8	—	—	23·9
131	0·094	0·091	41·8	19·3	—	—	22·6
						Mean:	23·3

* Concns., and, where necessary, rate-constants are corrected for thermal expansion of the solvent.
† The mixed solvent was prepared by making 10·0 ml. of water up to 100·0 ml. with 91·6 ml. of ethanol at 20°, there being a contraction of 1·6 ml. on mixing.

solvent. Three of them relate to methylmercuric–mercuric exchange reactions involving anions other than bromide, *viz.*, the exchanges;

$$MeHgX + \overset{*}{H}gX_2 \rightleftharpoons Me\overset{*}{H}gX + HgX_2,$$

where X = I, OAc, and NO_3 severally. The motive here was to set up a distinction, by comparison of the absolute rates of mercury exchanges with different anions, between the two second-order mechanisms of one-alkyl electrophilic substitution, S_E2 and S_Ei, as was done for the two-alkyl [7] and three-alkyl substitutions.[8] It was necessary to know, for any reactions thus to be compared as to rate, that their kinetic forms were the same.

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We also report here on the kinetic effect of changing the alkyl groups from methyl to s-butyl. The motive now was to prepare the way for a correlated stereochemical investigation with an optically active s-butylmercuric salt. Charman had made [9] a preliminary kinetic examination of the three exchange reactions,

$$Bu^sHgBr + H\overset{*}{g}Br_2 \rightleftharpoons Bu^s\overset{*}{H}gBr + HgBr_2$$

$$Bu^sHgI + H\overset{*}{g}I_2 \rightleftharpoons Bu^s\overset{*}{H}gI + HgI_2$$

$$Bu^sHg{\cdot}OAc + H\overset{*}{g}(OAc)_2 \rightleftharpoons Bu^s\overset{*}{H}g{\cdot}OAc + Hg(OAc)_2$$

and concluded that the first two of them are appropriate neither for a more extended kinetic study, nor, therefore, for correlated stereochemical work, because side-reactions, leading to insoluble (probably mercurous or other polymeric) salts, set in too early. On the other hand, the acetate reaction gave him no serious trouble on account of side-reactions, though these do occur in protracted experiments; and it is on the basis of that knowledge that we have developed a correlated kinetic and stereochemical study of this substitution. In this Section, we report the determination of its kinetic form.

The rate-constants on which all these additional determinations of kinetic form depend are collected in Table 2. They are all for reactions in ethanol, except that the methyl-group–nitrate-ion reaction was conducted in ethanol containing a small amount of nitric acid (and a kinetically scarcely significant amount of water) in order to secure complete solubility and stability of the reactants at the temperature and concentrations used. The reactions were not all studied at the same temperature, because some of them go inconveniently fast at one or both of the temperatures, 100° and 60°, used in the work reported in Section 2 on the methyl-group–bromide-ion reaction. The temperatures, however, are immaterial to the determination of kinetic form. And, since the temperature-coefficient of the rate in ethanol of the methyl-group–bromide-ion reaction is known (Section 2), the temperature differences offer no obstacle to the intended comparison of the widely separated rates we find. As before, our label of radioactivity was initially in the mercuric salt.

In all these cases, the second-order two-alkyl-substitution rate-constant, $k_2^{(2)}$, and also the first-order one-alkyl constant, $k_1^{(1)}$, vary systematically with reactant concentration, and only the second-order one-alkyl constant, $k_2^{(1)}$, remains invariant with changing concentrations to within the observational error. Therefore, all these reactions, including the one of which we have studied the stereochemistry, must be one-alkyl substitutions going in a single step of unit molecularity in each reactant. Thus, as far as this test shows, they can fairly be considered together with respect to mechanism.

(4) *Salt Effects on the One-alkyl Substitution.*—We have to start this Section with a pre-view of some conclusions, in order to explain its scope, and, incidentally, why the word " uncatalysed " occurs in the title of this paper, and in those of some of its Sections. Our finding is that, phenomenologically, the one-alkyl mercury-exchange displays two kinetic salt effects, both positive, but of very different magnitudes. One is small enough to be understood as a normal (or primary) salt-effect, essentially a form of medium effect. The other is specific to certain anions, such as halide ions, which co-ordinate with mercuric salts; and this effect is so powerful that it can justly be described as a " catalysis," thus implying the incursion of a new mechanism. We report here only the " normal " salt effect, the object being to secure some further indication of the mechanism of the " uncatalysed " reaction, with which alone this paper is concerned. The " catalytic " effect, importing, as it does, a completely separate mechanistic problem, is considered in the following paper.

It was reported in Part III [8] that added lithium nitrate induced weak comparable accelerations, obviously normal salt effects, on the two three-alkyl exchanges thus studied, *viz.*, those of s-butylmercuric bromide and nitrate with di-s-butylmercury. We therefore

[9] Charman, Thesis, London University, 1958, p. 82.

examined the kinetic effects of lithium nitrate on two of our one-alkyl exchanges, *viz.*, those of methylmercuric bromide with mercuric bromide and of s-butylmercuric acetate

TABLE 2. *First-order rate-constants of label-transfer (k_1^{Hg} in sec.$^{-1}$), rates of mercury exchange (k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$) and first-order ($k_1^{(1)}$ in sec.$^{-1}$) and second-order ($k_2^{(2)}$ and $k_2^{(1)}$ in mole^{-1} l. sec.$^{-1}$) rate-constants of substitutions by mercuric salts (concentration a) in alkylmercuric salts (concentration b).**

Run	*a* (M)	*b* (M)	$10^5k_1^{Hg}$	$10^6k_0^{Hg}$	$10^4k_2^{(2)}$	$10^5k_1^{(1)}$	$10^4k_2^{(1)}$
Methylmercuric bromide and mercuric bromide in ethanol							
Table 1	Various	Various	Various	Various	—	Mean (100·2°)	1·28
"	"	"	"	"	—	Mean (59·8°)	0·050
Methylmercuric iodide and mercuric iodide at 100·2° in ethanol							
49	0·048	0·122	17·5	6·03	4·07	4·97	10·3
56	0·0234	0·122	13·4	2·63	1·76	2·15	9·2
58	0·0211	0·127	15·8	2·87	1·78	2·26	10·7
73	0·073	0·045	12·7	3·25	16·1	7·24	9·9
74	0·073	0·136	21·7	10·3	5·58	7·59	10·4
						Mean:	10·1
Methylmercuric acetate and mercuric acetate at 59·8° in ethanol							
120	0·320	0·058	197	96·5	287	166	52
111	0·0466	0·058	46·0	11·8	35·4	20·5	44
116	0·0762	0·059	70·3	23·4	67·2	39·6	52
119	0·320	0·153	246	255	109	166	52
						Mean:	50
s-Butylmercuric acetate and mercuric acetate at 59·8° in ethanol							
92	0·069	0·104	5·33	2·21	2·09	2·17	3·08
93	0·114	0·120	6·37	3·72	2·58	3·10	2·72
102	0·127	0·090	3·73	3·65	4·50	4·05	3·19
104	0·119	0·247	12·2	9·79	1·60	3·96	3·33
117	0·104	0·325	14·0	11·1	1·05	3·38	3·25
118	0·038	0·341	10·4	3·56	0·306	1·04	2·75
						Mean:	3·05
Methylmercuric nitrate and mercuric nitrate at 0·0° in ethanol containing nitric acid (0·32M) and water (0·8%)							
85	0·125	0·098	35·0	19·2	20·0	19·6	15·7
86	0·117	0·195	53·4	39·0	10·3	10·0	17·1
87	0·223	0·185	71·8	72·7	21·2	39·2	17·6
88	0·140	0·299	75·1	71·6	8·01	23·9	17·1
						Mean:	16·9

* Concentrations and rate-constants are corrected where necessary for thermal volume changes of the solvent.

with mercuric acetate. The radioactive label was, as usual, initially in the mercuric salt. The results are summarised in Table 3.

Lithium nitrate exerts mild accelerating effects on both reactions, a larger one on the methyl-group–bromide-ion reaction than on the s-butyl–acetate reaction; but in both, the order of magnitude is the same as that of the effects observed on the two three-alkyl reactions examined. In the bromide reaction, the logarithm of the rate increases linearly with the concentration of added salt. In the acetate reaction, the logarithm rises with a power of concentration which lies below unity but well above one-half. The significance of these results will be considered in Section 6.

(5) *Stereochemical Course of the Uncatalysed One-alkyl Substitution.*—For a study of the stereochemical course of any reaction, one needs clean stoicheiometry and well-defined kinetics. The only one of the three examined reactions of s-butyl compounds (Section 3)

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which was free enough from side-reactions to fulfil this pre-requisite was that of s-butylmercuric acetate with mercuric acetate. This reaction goes in ethanol at 59·8°, without measurable disturbance, for at least 2—3 half-lives, say 80% of reaction, which is about as far as the radiometric kinetics could in any case be followed accurately. Nevertheless

TABLE 3. *Effects of added lithium nitrate on the second-order rate-constants of substitution ($k_2^{(1)}$ in mole^{-1} l. sec.$^{-1}$) by mercuric salts in alkylmercuric salts in ethanol.**

Run	*a* (M)	*b* (M)	[$LiNO_3$] (M)	Mean	$10^4k_2^{(1)}$	Mean
Methylmercuric bromide and mercuric bromide at 100·2°						
Table 1	Various	Various	0·0	0·0	—	1·28
60B	0·091	0·091	0·048	0·048	1·83	1·92
71	0·091	0·091	0·048		2·00	
72	0·091	0·091	0·091	0·096	3·22	3·33
25	0·100	0·100	0·100		3·44	
60A	0·091	0·091	0·133	0·133	4·73	4·73
s-Butylmercuric acetate and mercuric acetate at 59·8°						
Table 2	Various	Various	0·0	0·0	—	3·07
113	0·109	0·117	0·115	0·115	4·58	4·58
112	0·105	0·131	0·222	0·222	5·40	5·40
107	0·116	0·143	0·341	0·341	6·00	6·00

* Concentrations and rate-constants are corrected for thermal expansion of the solvent.

there is a very slow decomposition, which, after about 7 half-lives (99% reaction) is shown by the accumulation of an appreciable, and after 40 half-lives, a very substantial, precipitate.

The exchanges with optically active s-butylmercuric acetate and mercuric acetate were run with each reactant in concentration 0·1M in ethanol at 59·8°, conditions in which the half-life is 3·1 hours. It was first shown that, with the mercuric acetate omitted, the s-butylmercuric acetate could be thus heated in ethanol for a period equal to 40 half-lives of the exchange reaction, without loss of optical activity, and, incidentally, without decomposition leading to a precipitate, such as accompanies the exchange reaction. The observed polarimetric effects accompanying the exchange reaction are noted in Table 4. In all these experiments, the optical activity of the s-butylmercuric salt, was measured in the bromide, precipitated from a solution of the acetate with potassium bromide.

TABLE 4. *Polarimetric changes accompanying the mercury-exchange reaction of optically active s-butylmercuric acetate with mercuric acetate in ethanol at* 59·8°.

([s-$\overset{\circ}{B}$uHg·OAc] = [$Hg(OAc)_2$] = 0·100M. Specific rotations, $[\alpha]_D^{20}$, in acetone, with $c = 4$, are of s-butylmercuric bromide, obtained from the acetate, either as used, or as in reaction samples.)

Run	Time (hr.)	½-lives	Reaction (%)	$[\alpha]_D^{20}$	Run	Time (hr.)	½-lives	Reaction (%)	$[\alpha]_D^{20}$
Initial	0	0	0	−5·7°	186	7·0	2·3	79·7	−5·6°
183	1·0	0·32	19·9	−5·4	184	26·5	8·6	99·7	−5·0
183	3·0	0·97	49·0	−5·6	185	27	8·7	99·7	−5·3
184	3·0	0·97	49·0	−5·5	186	120	39	100·0	−1·3
185	6·0	1·9	73·2	−5·9					

We see that the rotation remains sensibly constant up to 2·3 half-lives, or 80% of reaction. It has fallen by only 10% after 8—9 half-lives, or 99·7% of reaction, when decomposition is beginning to be obvious. Most of it has gone after 39 half-lives when the decomposition has become extensive. Clearly, the fall of rotation at these late times is to do with the decomposition, and the exchange reaction itself has no effect on rotation. We conclude that configuration is fully preserved in this exchange reaction.

(6) *Mechanism of the Uncatalysed One-alkyl Substitution.*—The kinetic results of Sections 2 and 3 show that all the mercury-exchange reactions considered in this paper

exemplify the one-alkyl substitution anticipated in Part I.[6] The same data show that this electrophilic substitution proceeds in a single step of unit order in each reactant, whilst the polarimetric results of Section 5 establish that in that step configuration is fully preserved. These findings agree in excluding mechanism S_E1, and in permitting either mechanism S_E2 or mechanism S_Ei. The problem remains of distinguishing between these two mechanisms: we have a bimolecular transition state, and have to decide whether it is an open or a closed one.

The simplest test of that matter is to increase the ionicity of the interacting salts and note the effect of so doing on the absolute rate. We find that from halides to acetate, and thence to nitrate, the rate increases sharply, indeed by factors of 10^2—10^3 at each step. This will be clear from the summary in Table 5 of second-order rate-constants for one-alkyl substitution, which establish the rate sequence, MeHgBr < MeHgI ≪ MeHg·OAc ≪ MeHg·NO_3. It is thus shown that the reaction receives no important assistance from combination between the anion of the substituting agent and the mercury atom being expelled, or, in other words, that the transition state is an open one, apart from its solvation. This conclusion is confirmed by the kinetic salt effects next to be discussed, and, for the bromide reactions, by the results in the next paper, which show what does happen when we take steps calculated to close the transition state.

TABLE 5. *Summary of second-order rate-constants* ($k_2^{(1)}$ *in mole*$^{-1}$ *l. sec.*$^{-1}$) *in ethanol of the one-alkyl electrophilic substitutions,* $RHgX + \overset{*}{H}gX_2 \longrightarrow R\overset{*}{H}gX + HgX_2$.

		$10^5k_2^{(1)}$			
R	X	100·2°	59·8°	0·0°	Rel. rate
Me	Br	12·8	0·50	0·0007 †	1
,,	I	101	—	—	7·9
,,	OAc	—	500	—	1000
,,	NO_3	—	—	169	240,000
Bu^s	OAc	—	30·5	—	61

† Extrapolated from observed values at the higher temperatures.

The positive salt effects reported in Section 4 show that, for both the bromide and acetate reactions thus examined, the transition states are more polar than the initial states. Thus, 0·1M of added lithium nitrate increases the rate of the former reaction by a factor of about 2·5, and of the latter by one of about 1·5. In the bromide reaction, the initial state is relatively non-polar, but the transition state must be much more polar. Furthermore, the semilogarithmic linearity of this salt effect suggests that the extra polarity of the transition state is one of stronger dipoles,[10,11] rather than of newly produced free ions. In the reaction of the more ionic acetates, the initial state is moderately polar, and the transition state is more polar still, but by a smaller margin than before. The functional form of the salt effect is now intermediate between those expected for ion–dipole and ion–ion interaction, and may be indicating that in the transition state, not only are dipoles further strengthened, but also rather more free ions are produced. All this is much easier to understand on the basis of an open than on that of a closed transition state.

Because of their analogous electrostatic origins, normal salt effects and polar co-solvent effects usually follow each other qualitatively, in the absence of specific effects, though differences of functional form will arise, if only because co-solvents must act at closer ranges than those at which salts may act. It is shown in Section 2 that the addition of water to the ethanolic solvent does accelerate the bromide reaction. But 10 vols. % of water raised the rate by a factor of only 1·8, an amount which, having regard to the considerable magnitude of the salt effect on the bromide reaction, seems small, until it is

[10] Kirkwood, *Chem. Rev.*, 1939, **24**, 2330.
[11] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 983.

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recollected that a countervailing specific effect of water is expected, which has to be overcome. For it is fairly certain that water specifically co-ordinates with mercuric halides,[12] perhaps four molecules of water, to give octahedral structures. Thus the formation of the transition state will necessitate a partial de-aquation, which, being endothermic, should of itself retard reaction.

The summary of these conclusions is that all the mercury exchanges here considered of simple alkylmercuric halides, acetates, and nitrates, with corresponding mercuric salts, exemplify the anticipated one-alkyl electrophilic mercury-for-mercury substitution, which proceeds by mechanism S_E2, with full retention of configuration.

Experimental

Materials.—Most of our methylmercuric bromide was prepared from methylmagnesium bromide and mercuric bromide, but some was made from dimethylmercury and mercuric bromide. The product obtained in either way had m. p. 161—162° (Found: C, 4·16; H, 0·95; Br, 27·2. Calc. for CH_3BrHg: C, 4·06; H, 1·02; Br, 27·1%). Nefedov and his co-workers [2] record m. p. 172°. We tried crystallisation from ethanol, methanol, ether, and benzene, and steam-distillation and sublimation, as alternative or successive methods of purification, but could not raise our m. p. above 161—162°, which essentially agrees with the m. p., 160°, recorded by earlier workers.[13,14] Our methylmercuric iodide was a gift from Imperial Chemical Industries Limited, through the courtesy of Dr. W. B. Waddington (Huddersfield): crystallised from ethanol, it had m. p. 144°. The acetate was made from dimethylmercury and mercuric acetate: [15] after sublimation it had m. p. 128—129°. s-Butylmercuric acetate was prepared analogously: [3] crystallised from pentane, it had m. p. 29°. The optically active salt was similarly obtained from optically active di-s-butylmercury.[7] Methylmercuric nitrate was prepared from methylmercuric bromide and silver nitrate: [16] crystallised from ether–pentane, it had m. p. 58—59°.

Radiomercuric oxide containing only ^{203}Hg and stable isotopes was converted with aqueous hydrobromic acid into radiomercuric bromide, which was crystallised from ethanol. Radiomercuric iodide was precipitated by potassium iodide from a solution of the oxide in aqueous nitric acid and was crystallised from aqueous dioxan. Radiomercuric acetate was made by dissolving the oxide in nitric acid, precipitating the hydrated oxide with potassium hydroxide, and dissolving the well-washed precipitate in dilute acetic acid, from which the acetate was crystallised. Radiomercuric nitrate was obtained by crystallisation from a solution of the oxide in aqueous nitric acid. The acetate and nitrate were dried in a vacuum over potassium hydroxide. Ethanol was dried by the method which uses ethyl phthalate.

Rates of Mercury Exchange.—Kinetics of the exchanges with bromides and iodides were followed by the sealed-tube method. The reaction solution was made up at 20°, and a charge of 10 ml. was enclosed in each tube. The tubes were placed in a thermostat, and, from time to time, one was transferred to a freezing-mixture. After an investigation of methods of separating alkylmercuric salts from mercuric salts, without entrainment of the latter, and without exchange during separation, a general procedure was evolved, which had to be modified slightly from case to case. For the exchange with methylmercuric bromide, the salts which had crystallised in the cooled tube, were, after opening of the tubes, caused to redissolve by heating to 20—30°. The solution was then poured through glass-wool into a continuously stirred 5% solution of potassium bromide in 50% aqueous ethanol. Pure methylmercuric bromide (m. p. and mixed m. p. 161—162°) was thus precipitated, usually at once, or, if not, after the addition of a little ice-water. For the exchange with methylmercuric iodide, it was found advisable to add some potassium iodide to the contents of the cooled tube, and then to complete re-dissolution by heating to 20° before pouring through glass wool into a stirred 10% solution of potassium iodide in 50% aqueous ethanol, pure methylmercuric iodide being precipitated.

The kinetic runs with acetates and nitrates were conducted in flasks, in which solutions

[12] Van Panthaleon van Eck, Thesis, Leiden University, 1958.
[13] Crymble, *J.*, 1914, **105**, 667.
[14] Vaughan, Spahr, and Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 4206.
[15] Sneed and Maynard, *J. Amer. Chem. Soc.*, 1922, **44**, 2942.
[16] Johns, Peterson, and Hixon, *J. Amer. Chem. Soc.*, 1930, **52**, 2820.

of the reactants, made separately at the reaction temperature, were mixed at that temperature. As methylmercuric nitrate is solvolysed in neutral ethanol, a small amount of nitric acid was added in the nitrate exchanges in order to obviate this difficulty. After known times in the thermostat, samples of 10 ml. were withdrawn to be run into empty tubes cooled with solid carbon dioxide–acetone. This method of quenching was shown to be adequate even for the rapid nitrate exchanges. For the acetate and the nitrate exchanges, the method of separation was as follows. To each cooled sample, 10 ml. of 10% aqueous potassium bromide were added. The precipitated mixture of methyl- or s-butyl-mercuric bromide and mercuric bromide was collected, washed, and dissolved in acetone. This solution was poured with stirring into 10 ml. of 10% aqueous potassium bromide, pure methyl- or s-butyl-mercuric bromide being precipitated

Weighed amounts of the recovered samples of methylmercuric bromide or iodide or s-butylmercuric bromide were dissolved each in 10 ml. of acetone, and the counts of radiation from these solutions were measured with precautions and corrections mentioned in the preceding paper.

The various rate-constants obtained by these methods are listed in Tables 1, 2, and 3. The methylmercuric bromide and iodide reactions at 100·2° were followed to about 70—85% of the possible extent of exchange, but the methylmercuric bromide reaction at 59·8° was followed only to 50—60% because appreciable decomposition set in during the long periods (weeks) needed to follow the reaction much further at this temperature. The methylmercuric acetate and nitrate reactions were followed to 70—80% of the possible amount of exchange: there was detectable decomposition in the later stages of these reactions, but not enough appreciably to affect the kinetics within the stated range. For the slower reactions of the s-butylmercuric salts, decomposition was generally more pronounced, and, for s-butylmercuric bromide and iodide, it made our rate-measurements too inaccurate to be quoted. However, the moderately fast reaction of s-butylmercuric acetate was followed up to 70—80% of the possible exchange (and the work of Section 5 suggests that it could probably have been followed somewhat further) without sensible disturbance from decomposition, though, here again, decomposition becomes considerable after long periods. It remains to record a few specimen runs, and this is done in Table 6.

TABLE 6. *Specimen runs.*

(In all runs the radioactivity was initially in a mercuric salt; and it was measured in samples of an alkylmercuric salt recovered after known reaction-times. The units of $k_2^{(1)}$ are mole^{-1} l. sec.$^{-1}$. These constants are corrected for the volume change of the solvent when the temperatures at which concentrations were set, and at which the reaction was conducted, were different.)

Run 30: [MeHgBr] = 0·100M, [$HgBr_2$] = 0·200M, at 20°; reaction in ethanol at 100·2°.

Time (hr.)	Count, MeHgBr (min.$^{-1}$, corr.)	Reaction (%) = 100 (1 − *f*)	$10^5k_2^{(1)}$ (corr.)
0	44·6	9·2	—
1	94·6	19·5	13·2
2	140·7	29·0	13·0
3	185·2	38·2	13·4
4	223·2	46·0	13·4
5	253·2	52·2	13·2
8	327·8	67·6	13·2
		Mean:	13·2

Run 117: [Bu^sHgOAc] = 0·325M, [$Hg(OAc)_2$] = 0·104M, at 60°; reaction in ethanol at 59·8°.

Time (min.)	Count, Bu^sHgBr (min.$^{-1}$, corr.)	Reaction (%) = 100 (1 − *f*)	$10^5k_2^{(1)}$
0	142·2	22·2	—
30	250·8	38·8	31·4
60	340·0	52·6	32·2
90	453·0	63·9	33·3
120	464·1	71·8	33·0
		Mean:	33·5

Run 87: [MeHg·NO_3] = 0·185M, [$Hg(NO_3)_2$] = 0·233M at 0°; reaction in ethanol containing 0·32M-nitric acid and 0·47M-water at 0·0°.

Time (min.)	Count, MeHgBr (min.$^{-1}$, corr.)	Reaction (%) = 100 (1 − *f*)	$10^5k_2^{(1)}$
8	105·2	26·4	(156)
12	155·3	39·0	168
18	216·1	54·3	177
25	268·3	67·3	182
34	306·8	77·1	177
		Mean:	176

Polarimetric Changes accompanying Mercury Exchange.—The optically active s-butylmercuric acetate (above) had $[\alpha]_D^{20}$ −4·5°, and the bromide obtained from it $[\alpha]_D^{20}$ −5·7° (*c* = 4,

in acetone). The conditions of the runs with the optically active acetate are specified in Section 5. From timed samples of 25 ml., rapidly cooled, and mixed with 25 ml. of 10% aqueous potassium bromide, s-butylmercuric bromide was precipitated, which was washed with potassium bromide solution, and with water, and, when dry, crystallised from pentane, before its rotation ($l = 2$ dm.) was measured in acetone ($c = 4$). The specific rotations, thus obtained after various reaction times in ethanol at 59·8°, are listed in Table 4.

A Ramsay Fellowship held by one of us (H. C. V.) is gratefully acknowledged.

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[*Received, September 20th*, 1960.]

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228. *Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part V.*[1] *Kinetics, Stereochemistry, and Mechanism of Anion-catalysed One-alkyl Mercury-exchange Reactions.*

By H. B. CHARMAN, E. D. HUGHES, SIR CHRISTOPHER INGOLD, and H. C. VOLGER.

Mercury-exchange between alkylmercuric and mercuric salts, as followed through transfer of radioactivity, is catalysed by anions which co-ordinate strongly with mercury. This is shown for iodide, bromide, chloride, and acetate, as catalysing anions, the catalysis diminishing in this order, and for methyl and s-butyl as alkyl groups. A kinetic study showed that, in general, two catalytic processes are concurrently at work; that both are one-alkyl electrophilic substitutions, bimolecular apart from the catalysis; but that in one, an extra anion is taken into the reacting system, and that in the other two extra anions are so included. These two catalytic processes can be separated in favourable cases, and, this having been done, it was shown, by work with optically active s-butylmercuric salts, that in each process stereochemical configuration is fully preserved. It is argued that both processes have cyclic transition states, and, indeed, are forms of the internal mechanism of electrophilic substitution, S_Ei, contemplated in Part I, and now observed for the first time.

(1) *The Basic Observation.*—The form of one-alkyl mercury-exchange here to be described is new, except for the brief mention of it in Part IV [1] Section 4, and the mention of its use to prepare a doubly-labelled alkylmercuric salt in Part III,[2] Section 6a. The basic observation is that, when, in a one-alkyl mercury-exchange with anions which co-ordinate well with mercury, a common-anion alkali-metal salt is added, the exchange undergoes an acceleration far beyond the scope of any medium effect. For example, the mercury-exchange between methylmercuric bromide and mercuric bromide, each, say, in 0·1M-concentration in ethanol, is accelerated by comparable concentrations of lithium bromide by factors of the order of 100. This is no normal salt-effect, analogous, say, to that of lithium nitrate or lithium perchlorate: we designate it as a catalysis, implying that a new mechanism has intervened. We have found such catalysis in one-alkyl mercury-exchanges with iodides, bromides, chlorides, and even acetates; and with methyl and s-butyl, as examples of alkyl groups. We report below the kinetics and stereochemistry of this catalysed reaction.

(2) *Kinetics of the Anion-catalysed One-alkyl Substitution.*—The kinetics have been studied most fully in the example of the following exchange reaction in ethanol at 60°:

$$MeHgBr + {}^{*}HgBr_2 \underset{}{\overset{LiBr}{\rightleftharpoons}} {}^{*}MeHgBr + HgBr_2$$

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[1] Part IV, Hughes, Ingold, Thorpe, and Volger, preceding paper.
[2] Part III, Charman, Hughes, Ingold, and Thorpe, *J.*, 1961, 1121.

where the asterisk denotes a label of radioactivity, that of ^{203}Hg. The rate data are in Table 1. The first-order rate-constant of label-transfer, k_1^{Hg}, is an experimental result, independent of any hypothesis concerning the kinetic form of the substitution; and so is the rate of exchange, $k_0^{Hg} = k_1^{Hg}ab/(a + b)$, where a and b are the concentrations of mercuric bromide and methylmercuric bromide, respectively. From these experimental constants, we can derive various rate-constants of substitution, according to our hypothesis of its kinetic form; but in fact we tabulate only the second-order rate-constant of one-alkyl substitution, $k_{2c}^{(1)} = k_0^{Hg}/ab$, calling it $k_{2c}^{(1)}$ (obs.), to distinguish it from the quantities, called $k_{2c}^{(1)}$ (calc.), which are calculated from a formula, derived below from a theory of the mechanism of the catalysis.

Several general points are apparent. First, the second-order rate-constant of one-alkyl substitution, $k_{2c}^{(1)}$ (obs.), is nearly invariant with changing concentration of methylmercuric bromide, when the other concentrations are kept constant. So, indeed, would

TABLE 1. *First-order rate-constants of label-transfer* (k_1^{Hg} *in sec.*$^{-1}$), *rates of exchange* (k_0^{Hg} *in mole l.*$^{-1}$ *sec.*$^{-1}$), *and second-order constants of one-alkyl substitution* [$k_{2c}^{(1)}$ (obs.) *in mole*$^{-1}$ *l. sec.*$^{-1}$] *by mercuric bromide* (*concentration a*) *in methylmercuric bromide* (*concentration b*), *under catalysis by lithium bromide* (*concentration c*), *as radiometrically determined by mercury-exchange in ethanol at* 59·8°.

[The radioactivity of ^{203}Hg was initially in the mercuric bromide. Concentrations and rate-constants are corrected for thermal expansion of the solvent. As to $k_{2c}^{(1)}$ (calc.), see Section 5.]

Run	*a* (M)	*b* (M)	*c* (M)	$10^6k_1^{Hg}$	$10^7k_0^{Hg}$	$10^5k_{2c}^{(1)}$ (obs.)	$10^5k_{2c}^{(1)}$ (calc.)
63, 69	0·095	0·095	0·000	0·92	0·44	0·49	—
55	0·095	0·095	0·035	24·3	11·6	12·8	12·9
76	0·095	0·095	0·065	40·8	19·4	21·5	23·9
52	0·095	0·095	0·105	74	35·2	39	40
53	0·095	0·095	0·161	131	52	69	68
62	0·095	0·095	0·203	167	79	88	89
67	0·095	0·095	0·203	171	81	90	89
70	0·095	0·095	0·271	230	109	121	123
59	0·095	0·095	0·311	277	132	146	143
61	0·176	0·095	0·193	141	87	52	44
68	0·252	0·095	0·206	125	86	36	29
64	0·291	0·095	0·205	127	91	33	25
66	0·095	0·158	0·204	190	112	75	89
69	0·095	0·190	0·214	216	137	76	94

be the first-order rate-constant of one-alkyl substitution, $k_1^{(1)} = k_0^{Hg}/b$. But since the unimolecular mechanism, corresponding to that constant, is excluded by the stereochemical results reported in Section 4, we do not consider the first-order constant further. The second-order constant of two-alkyl substitution, $k_2^{(2)} = k_0^{Hg}/b^2$, is not invariant with any concentration, and hence two-alkyl substitution is excluded. Moreover, since we know [3] that two-alkyl substitution is strongly retarded by lithium bromide, that process is excluded by the catalysis. Neither, therefore, shall we consider that constant any further.

Secondly, as can be seen from the plot in the Figure, the second-order rate-constant of one-alkyl substitution, $k_{2c}^{(1)}$ (obs.)—the constant itself, not its logarithm, as would be more relevant to the consideration of normal salt-effects—increases linearly with the concentration of lithium bromide over considerable ranges, when the other concentrations are kept constant. Moreover, the gradient of linear increase becomes larger rather sharply when the concentration of lithium bromide exceeds that of mercuric bromide. Thirdly, when this is so, then, for a constant concentration of lithium bromide, the second-order constant, $k_{2c}^{(1)}$ (obs.), becomes much reduced on increasing the concentration of mercuric bromide. It seems also to be reduced, though only slightly, on increasing the concentration of methylmercuric bromide.

Though we shall develop the theory of the catalysis in more detail in Section 5, the

[3] Charman, Hughes, and Ingold, *J.*, 1959, 2530.

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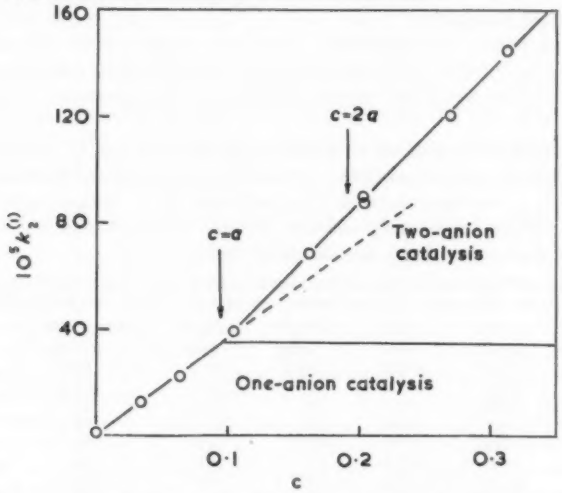
general nature of what is happening will already be obvious. As long as the concentration of lithium bromide is less than that of mercuric bromide, we observe a single catalysis, depending on a transition state of reduced free-energy; and this transition state could be, and no doubt mainly is, produced from the molecule MeHgBr and the anion $HgBr_3^-$, the latter preformed nearly stoicheiometrically from $HgBr_2$ and Br^-. When the concentration

Dependence of second-order rate-constants of one-alkyl substitution, $k_{2c}^{(1)}$, by mercuric bromide in methylmercuric bromide in ethanol at 59·8°, on the concentration (c) of added lithium bromide, the concentrations (a and b) of the mercury-exchanging substances being 0·095M.



The curve is that of equation (i), p. 1148, *with* $10^5\kappa_1 = 35$ *mole*$^{-1}$ *l. sec.*$^{-1}$ *and* $10^5\kappa_2 = 500$ *mole*$^{-2}$ *l.*^{2} *sec.*$^{-1}$. *The positions marked* $c = a$ *and* $c = 2a$ *are where breaks should occur according to different assumptions that might be made for the purpose of deriving a theoretical equation* (*cf. Section* 5).

of lithium bromide exceeds that of mercuric bromide, then a second and superposed catalysis comes under observation, involving a transition state of slightly lower free-energy still; and this second transition state could be, and may largely be, produced from the two anions $HgBr_3^-$ and $MeHgBr_2^-$ provided that, after preformation of the former is complete, that of the latter proceeds to only a small equilibrium extent.* It is convenient to name these two types of catalysis " one-anion " and " two-anion " catalysis.

(3) *Kinetics: Generalisation to Other Anions and Another Alkyl Group.*—It was obviously necessary to establish the scope of anion catalysis, and to confirm, if possible, its suspected dependence on the power of the anion to co-ordinate with mercury. We have found specific catalysis by iodide, bromide, chloride, and acetate ions, diminishing in that order; but none by acetic acid molecules, and none, as was shown in Part IV,[1] by nitrate ions.

Since two new types of transition state were clearly involved in these catalysed reactions, we had to contemplate two new and independent tasks of establishing the stereochemical course of the substitution under catalytic conditions, known as to kinetic form. Therefore, in order to build up the necessary kinetic background, we changed, in

* This last conclusion may need a further word. All pre-equilibrium complexings must be either slight, or almost complete, in order to account for the linearities. If the second complexing were nearly complete, a second break would appear where the concentration of lithium bromide equals the sum of those of the mercuric and methylmercuric bromide—exactly as the near-completeness of the first complexing leads to the break we find. Therefore, our curve shows that, whilst the first complexing is nearly complete, the second is only slight.

these further kinetic studies, from methyl to s-butyl systems, such as could afterwards be examined in optically active form.

The following mercury-exchange reactions have been studied kinetically, by the transfer of radioactivity, due to ^{203}Hg, from the mercuric to the s-butylmercuric salt:

$$Bu^sHgI + \overset{*}{Hg}I_2 \overset{KI}{\rightleftharpoons} Bu^s\overset{*}{Hg}I + HgI_2$$
$$Bu^sHgBr + \overset{*}{Hg}Br_2 \overset{LiBr}{\rightleftharpoons} Bu^s\overset{*}{Hg}Br + HgBr_2 \quad \text{acetone at 35°}$$
$$Bu^sHgCl + \overset{*}{Hg}Cl_2 \overset{LiCl}{\rightleftharpoons} Bu^s\overset{*}{Hg}Cl + HgCl_2$$

$$Bu^sHg{\cdot}OAc + \overset{*}{Hg}(OAc)_2 \overset{LiOAc}{\rightleftharpoons} Bu^s\overset{*}{Hg}{\cdot}OAc + Hg(OAc)_2$$
$$Bu^sHg{\cdot}OAc + \overset{*}{Hg}(OAc)_2 \overset{HOAc}{\rightleftharpoons} Bu^s\overset{*}{Hg}{\cdot}OAc + Hg(OAc)_2 \quad \text{ethanol at 60°}$$

The various rate-constants for these reactions are collected in Table 2.

TABLE 2. *First-order rate-constants of label-transfer (k_1^{Hg} in sec.$^{-1}$) rates of exchange (k_0^{Hg} in mole l.$^{-1}$ sec.$^{-1}$) and second-order rate-constants of one-alkyl substitution ($k_{2c}^{(1)}$ in mole^{-1} l. sec.$^{-1}$) by mercuric salts (concentration a) in s-butylmercuric salts (concentration b) with added alkali-metal salts or acetic acid (concentration c).*

[The radioactive label was initially in the mercuric salt. Concentrations were set at the reaction temperatures, and hence no corrections for thermal expansion are necessary. As to $k_{2c}^{(1)}$ (calc.) see Section 5.]

Run	*a* (M)	*b* (M)	*c* (M)	$10^6k_1^{Hg}$	$10^7k_0^{Hg}$	$10^5k_{2c}^{(1)}$ (obs.)	$10^5k_{2c}^{(1)}$ (calc.)
	s-Butylmercuric iodide, mercuric iodide, and potassium iodide, in acetone at 35·0°						
205	0·050	0·150	0·000	0·00	0·00	0·00	—
211	0·045	0·135	0·0056	1·42	0·48	0·79	0·62
212	0·045	0·135	0·0224	4·14	1·40	2·30	2·49
210	0·041	0·163	0·0120	2·49	0·82	1·22	1·46
207	0·053	0·163	0·056	18·6	7·4	8·6	6·2
209	0·053	0·163	0·112	56·9	22·7	26·3	28·6
208	0·106	0·163	0·112	16·4	10·6	6·1	7·4
	s-Butylmercuric bromide, mercuric bromide, and lithium bromide, in acetone at 35·0°						
201	0·300	0·300	0·000	0·00	0·00	0·00	—
214	0·022	0·201	0·244	5·00	0·99	2·25	2·00
213	0·028	0·196	0·275	4·48	1·00	2·00	2·13
	s-Butylmercuric chloride, mercuric chloride, and lithium chloride, in acetone at 35·0°						
200	0·150	0·350	0·000	0·00	0·00	0·00	—
215	0·090	0·204	0·468	0·94	0·58	0·32	0·30
	s-Butylmercuric acetate, mercuric acetate, and lithium acetate, in ethanol at 59·8°						
102	0·090	0·127	0·000	37·3	36·5	32	—
109	0·101	0·112	0·0465	308	164	145	124
114	0·105	0·110	0·0968	455	244	211	216
115	0·105	0·102	0·148	450	250	217	232
	s-Butylmercuric acetate, mercuric acetate, and acetic acid, in ethanol at 59·8°						
102	0·090	0·127	0·000	37·3	36·5	32	—
105	0·101	0·137	0·113	83·3	47·0	35	—
106	0·123	0·140	0·349	86·2	56·5	33	—

The strongest catalysis here is by the alkali-metal iodide on the exchange of s-butylmercuric and mercuric iodides. The figures are not suitable for graphical representation, but an analysis of them (Section 5) shows that we have again both one-anion and two-anion catalysis. And again, the effectiveness of the two-anion catalysis is reduced when, with the concentration of alkali-metal salt in excess over that of the mercuric salt, the latter concentration is increased. The catalysis generally falls off along the series, iodides,

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bromides, chlorides, acetates. In the exchange of s-butylmercuric and mercuric acetates, as affected by the alkali-metal acetate, the one-anion catalysis, though undoubtedly specific, is relatively mild, and the two-alkyl catalysis is inappreciable, the rates rising to a limit as the concentration of catalyst equals and surpasses that of the mercuric salt. In the same exchange, in the absence of an alkali-metal salt, but in the presence of acetic acid, no catalysis is apparent.

(4) *Steric Course of the One- and Two-anion-catalysed One-alkyl Substitutions.*—One-alkyl catalysis was stereochemically investigated in the example of the exchange reaction of optically active s-butylmercuric iodide with mercuric iodide in acetone, in the presence of a concentration of potassium iodide equal to that of the mercuric iodide. Practically the whole of the reaction is then of the one-anion-catalysed type. As shown in Table 3, the s-butylmercuric iodide recovered after two half-lives had its optical activity completely unchanged.

Two-alkyl catalysis was similarly examined in the exchange reaction of optically active s-butylmercuric bromide with mercuric bromide in acetone, in the presence of lithium bromide in an excess of the order of 10-fold over the mercuric bromide. Nearly the whole of the reaction now proceeds by the two-anion-catalysed mechanism. The same stereochemical result was obtained; and it was used preparatively in order to produce the optically active and radioactive s-butylmercuric bromide required for use in the work of Part III.[2] Some of these runs were followed for very long periods, the longest that of the second run recorded in Table 3

TABLE 3. *Initial and final optical rotations of s-butylmercuric halides in exchange reactions with mercuric halides under catalysis by alkali-metal halides in acetone at* 35·0°.

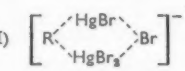
(The concentrations *a*, *b*, and *c*, have the significance given in the heading of Table 2. Specific rotations $[\alpha]_D^{20}$ are for $c = 5$, in acetone; X = I or Br.)

Run	*a* (M)	*b* (M)	*c* (M)	½-lives followed	$[\alpha]_D^{20}$ of Bu^sHgX initial	final
One-anion catalysis: $Bu^sI + HgI_2 + KI$						
220	0·1	0·1	0·1	2	+3·4°	+3·4°
Two-anion catalysis: $Bu^sBr + HgBr_2 + LiBr$						
230	0·2	0·2	1·7	200	+4·5°	+4·5°

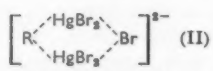
It follows from these polarimetric results that both the one-anion and the two-anion mechanisms of one-alkyl mercury-exchange preserve stereochemical configuration completely.

(5) *Mechanisms of the Anion-catalysed One-alkyl Substitutions.*—Let us first consider the broad picture of known specific salt effects on electrophilic mercury-for-mercury substitutions, as disclosed in Parts II [3] and III [2] and in this paper, using the behaviour of lithium bromide as example. We seek to understand why the two-alkyl substitution of mercuric bromide in a dialkylmercury is so strongly retarded by lithium bromide that an amount of it equivalent to that of the mercuric bromide practically puts the latter out of action; whereas in the three-alkyl substitution of an alkylmercuric bromide in a dialkylmercury, lithium bromide exerts at most only a small specific retardation—small enough to be difficult to disentangle from the general salt effect; and yet, in the one-alkyl substitutions of mercuric bromide in alkylmercuric bromides, we find lithium bromide conferring the great accelerations here described. We think the explanation must be that a bromide ion can co-ordinate strongly with mercuric bromide, weakly with an alkylmercuric bromide, and not at all with a dialkylmercury. Then, in the two-alkyl substitution, the bromide ion will combine strongly with the initial state to form the anion $HgBr_3^-$, but only weakly with the transition state, in which the mercury of the original

mercuric salt has in part become an alkylmercuric mercury atom: hence the strong retardation. In the three-alkyl substitution, the bromide ion can combine only weakly with the initial state, and still more weakly or not at all with the transition state; hence the quite trivial retardation. In the one-alkyl substitution, the bromide ion can combine strongly with the initial state, again to form $HgBr_3^-$, but more strongly with the transition state, in which it can bridge the mercury atoms, gaining stability by partial substitution of very stable $HgBr_2$–molecule bonding for much less stable $HgBr_3^-$–ion bonding.[5] The bromide ion not only can, but *must* bridge, because it enters, as $HgBr_3^-$, with the lower Hg of formula (I), and leaves, as $HgBr_2$, with the upper one; and hence it must be on its way from one mercury to the other in the transition state. We thus describe what our kinetics distinguish as one-anion catalysis: it implies the closed transition state (I), and exemplifies the internal mechanism of electrophilic substitution, S_Ei, which was anticipated in Part I,[4] and is now found for the first time.

(I) 

Transition state for one-anion catalysis

 (II)

Transition state for two-anion catalysis

One bromide ion having thus been taken into the reacting system, a second bromide ion could, and, as our kinetics show, does, in part, intervene. This second bromide ion could combine in the initial state to form either $HgBr_4^{2-}$, or $RHgBr_2^-$, or both, and with transition state (I) to form transition state (II), which might thus express the course of two-anion catalysis. It would be difficult to predict whether this second bromide ion should be bound in the initial or in the transition state the more strongly. Thus, in solution, as we point out below, $HgBr_2$ and Br^- combine to form $HgBr_3^-$ considerably more exothermally than $HgBr_3^-$ and Br^- combine to form $HgBr_4^{2-}$. But how uptake of the last bromide ion to produce one free $HgBr_4^{2-}$ ion in the initial state compares thermodynamically with its uptake to give two partly freed $HgBr_3^-$ ions in transition state (II), cannot be foreseen. If there were nothing to choose, and if also the alternative site in $RHgBr_2^-$ for the last-added bromide ion in the initial state were so unfavourable that it could be disregarded, then our one-anion and two-anion catalyses would have been just equally strong, and the latter, despite its presence and importance, could not have been distinguished by the simple method illustrated in the Figure. But the two-anion catalysis is somewhat the stronger, and is detected by this character. We conclude that the last-added bromide ion is actually combined somewhat more strongly in transition state (II) than in the corresponding initial state.* Transition state (II) thus represents the observed two-cation catalysis, which provides a second example of the expected mechanism S_Ei.

Though they are explained above with reference to catalysis by bromide ion, we regard these mechanisms as applicable to all the one-anion and two-anion catalyses described in this paper. In the case of acetate ion, only one-anion catalysis appears. It does not logically follow, but it is possible that this anion uses both its oxygen atoms to close the cyclic transition state.

One could gain the impression from some books that, among complex mercury halides, the doubly charged ones, HgX_4^{2-}, are more stable than the singly charged, HgX_3^-, for the same halogen. But this idea may arise in part from a reversal in the solid state of the balance of intrinsic molecular stability, by the greater lattice energies of salts of the doubly

* Since this was written, we have found a case in which two-anion catalysis is the weaker, so that the two-line curve, corresponding to that shown here, exhibits a decrease of gradient, instead of an increase, at the break.

[4] Charman, Hughes, and Ingold, *J.*, 1959, 2523.

[5] Sillén, *Acta Chem. Scand.*, 1949, **3**, 539; Marcus, *ibid.*, 1957, **11**, 599; Van Panthaleon van Eck, Thesis, Leiden University, 1958.

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charged ions. However that may be, our kinetic results, like those of Part II,[3] show clearly that, in dilute solution in ethanol or acetone at least, HgX_3^- is the dominant complex ion.

In an Appendix (p. 1149) we develop a two-constant kinetic equation for one-alkyl substitutions which are concurrently under one-anion and two-anion catalysis. In terms of our already-defined rate-constant of substitution, $k_{2c}^{(1)}$, it is

$$k_{2c}^{(1)}\ (\text{calc.}) = \left\{\begin{matrix} \kappa_1\, c/a & (c < a) \\ \kappa_1 + \kappa_2(c - a) & (c > a) \end{matrix}\right\} \quad . \quad . \quad . \quad . \quad . \quad (\text{i})$$

The curve shown, of two linear branches with a break at $c = a$, is a curve of this equation. Now one can see without calculation that the curve could not have that form unless progressively added lithium bromide were at first taken up nearly completely to form $HgBr_3^-$, until an excess of lithium bromide remained, and unless also this excess then entered into combination, *e.g.*, to form $HgBr_4^{2-}$, only to a small equilibrium extent. Consider some alternatives. If the excess of lithium bromide, after $HgBr_3^-$ had been fully formed, were taken up practically completely to form $HgBr_4^{2-}$, then the curve would become horizontal beyond $c = 2a$; *i.e.*, we should see a curve of three linear branches. If $HgBr_4^{2-}$ were so very stable that nearly all the lithium bromide went to form that ion, rather than the ion $HgBr_3^-$, from the beginning, then no break should occur at $c = a$, but the curve should turn horizontally at $c = 2a$; *i.e.*, we should have a two-branch curve with a break of the wrong form in the wrong place. In situations intermediate between the three limiting ones already considered, the linearities would be lost. Evidently, the bromide ion added as lithium bromide is stored nearly to the stoicheiometrically possible extent as $HgBr_3^-$ throughout our experimental range. This interpretation agrees with and includes, the assumption which had to be made in order to account for the kinetics of the anticatalysis by lithium bromide of the two-alkyl substitution treated in Part II.*

Collateral evidence on the relative stabilities of the singly and doubly charged complex halides of mercury relates largely to solvent water, wherein solvation heat, analogously to the lattice energy, may favour the doubly charged species. However, even here the singly charged ions seem to predominate. Garrett [6] could interpret the solubility of mercuric bromide in aqueous potassium bromide with the aid of a good equilibrium constant for complex formation, only on the basis that the complex was $HgBr_3^-$, though it is allowed that a little $HgBr_4^{2-}$ may be formed when both Br^- and $HgBr_3^-$ are in high concentration. Delwaulle and her collaborators showed [7] that the one-band Raman spectrum of $HgBr_2$ is almost completely replaced by a different spectrum, one of two bands, as would be expected for $HgBr_3^-$, assuming analogy with BF_3, when, in aqueous or ethanolic solution, one equivalent of an alkali bromide is added; and that, on the addition of a second equivalent, no similarly distinct new spectrum appears, but the two bands merely undergo shifts, such as might arise from the electrostatic effect of ambient ions, rather than from the incursion of a new spectral source in $HgBr_4^{2-}$, which should produce a four-band spectrum.† It has been shown,[5] both theoretically and practically, that the enthalpy and free-energy of binding of the last bromide ion in $HgBr_4^{2-}$ in water is considerably smaller than that of the last in $HgBr_3^-$, and is insufficient to hold $HgBr_4^{2-}$ together to any great extent except in very concentrated solutions.

* One of two criteria, used in Part II [3] to distinguish mechanisms S_E2 and S_Ei in two-alkyl exchange, was that, with bromides as reactants, complexing with lithium bromide theoretically should decrease an S_E2 rate (as it does the observed rate), but " might well " (as we put it) increase an S_Ei rate. We can now eliminate the slight reserve from this last statement, because we know observationally now, as we did not then, that such complexing does indeed increase S_Ei rates in systems suited to the formation of cyclic transition states.

† This interpretation is slightly different from that of the authors, who seem not to have considered the selection rules.

[6] Garrett, *J. Amer. Chem. Soc.*, 1939, **61**, 2744.

[7] Delwaulle, François, and Wiemann, *Compt. rend.*, 1938, **106**, 1100.

To return to equation (i): we can choose constants, κ_1 and κ_2, as in Table 4, and from them deduce the values of $k_{2c}^{(1)}$ (calc.) which are in the last columns of Tables 1 and 2. Comparison with $k_{2c}^{(1)}$ (obs.) reveals general agreement, but also some systematic deviations (Table 1, near the bottom). These are just such as would be expected if two of the assumptions, which we had to make (Appendix) in order to reduce the number of disposable constants to two, were not quite correct; in particular, if $HgBr_3^-$ were not formed quite stoicheiometrically, and if the formation of $RHgBr_2^-$ were not quite inappreciable. We have already noted other indications that both these things are true. Of course, we could make the relevant allowances theoretically, and so obtain a nearly perfect fit between theory and experiment; but this would entail the introduction of two more disposable constants.

The catalytic constants, κ_1 and κ_2, depend on reactant-structure, solvent, and temperature jointly; but the ratio κ_2/κ_1 should be more simply related to the affinity of the catalysing anion for mercury. The order of affinity thus indicated is I > Br > OAc. Van Panthaleon van Eck's binding energies of halide ions with mercury [5] give the order I > Br > Cl.

The two mechanisms of mercury-for-mercury substitution, epitomised in the transition-state formulæ (I) and (II), obviously require retention of stereochemical configuration.

TABLE 4. *Catalytic constants for one- and two-anion-catalysis (κ_1 in mole^{-1} l. sec.$^{-1}$ and κ_2 in mole^{-2} l.^{2} sec.$^{-1}$) by the anion* X *in one-alkyl substitutions by* HgX_2 *in* RHgX

Solvent	Temp.	R	X	$10^5\kappa_1$	$10^5\kappa_2$	κ_2/κ_1
Acetone	35·0°	Bu^s	I	5	400	80
,, ...	,,	,,	Br	Small	9	—
,, ...	,,	,,	Cl	Small	0·8	—
Ethanol	59·8	Me	Br	35	500	14
,, ...	,,	Bu^s	OAc	200	Small	~0

As is shown in Section 4, configuration is fully retained in both the one-anion- and the two-anion-catalysed substitutions.

Our general conclusion is that the mercury exchanges of mercuric salts with alkylmercuric salts, when specifically catalysed by anions which can co-ordinate with the mercury atoms, use forms of the internal mechanism of electrophilic substitution, S_Ei, contemplated in Part I.[4]

EXPERIMENTAL

Materials.—The sources of the substances here used have been noted in Parts I—IV.[1-4] with the exception of s-butylmercuric chloride and iodide. The chloride, which was precipitated at first as an oil on addition of aqueous hydrochloric acid to a solution in acetone of s-butylmercuric hydroxide,[4] had m. p. 29° when crystallised from ethanol. The iodide, which separated as a solid when aqueous potassium iodide was added to the acetone solution of hydroxide, had m. p. 52° after crystallisation from ethanol; it became yellow on storage in ordinary conditions, and was therefore kept at 0° in the dark, and was crystallised from pentane just before use.

Kinetics.—The methods of starting and stopping runs, of separating products from timed samples for radiometric or polarimetric examination, and the methods of these examinations, have been described in Part IV.[1] The conditions of the runs, and the rate-constants obtained, are given in Tables 1 and 2 above. We do not here record a specimen run, as any of our runs would be closely similar to one of those recorded as specimens in Part IV.[1]

APPENDIX

A full mass-law derivation of the rate equation for anion-catalysed one-alkyl mercury exchange would involve four equilibrium constants of complex formation (stability constants), and five rate-constants for individual substitutions of the complexes—a ridiculous number of disposable constants. We have therefore assumed the equilibrium constants of complex formation to be either very large or very small, as indicated by the reversed-arrow signs below.

This has the effect, not only of simplifying the algebra, but also of bunching the nine constants into two sets, with some constants belonging to both sets, which we can then replace by two omnibus constants, so reaching a formula which has some meaning in application to observational data.

The catalytic anion being X^-, the four complexing equilibria are taken to be strongly unbalanced, with equilibrium constants as follows:

$$X^- + HgX_2 \overset{K_1}{\rightleftharpoons} HgX_3^-$$
$$X^- + HgX_3^- \overset{K_2}{\rightleftharpoons} HgX_4^{2-}$$
$$X^- + RHgX \overset{K_3}{\rightleftharpoons} RHgX_2^-$$
$$X^- + RHgX_2^- \overset{K_4}{\rightleftharpoons} RHgX_3^{2-}$$

These equilibria lead to equilibria with the following constants, between five possible pairs of reactants for substitution:

$$\underbrace{RHgX + HgX_3^-}_{A} \overset{K_3/K_1}{\rightleftharpoons} \underbrace{RHgX_2^- + HgX_2}_{B}$$

$$\underbrace{RHgX + HgX_4^{2-}}_{C} \overset{K_3/K_2}{\rightleftharpoons} \underbrace{RHgX_2^- + HgX_3^-}_{D} \overset{K_4/K_1}{\rightleftharpoons} \underbrace{RHgX_3^{2-} + HgX_2}_{E}$$

For brevity, we designate the reactant pairs A—E, and define the respectively relevant second-order rate-constants of substitution as follows:

$$\text{Contributions to one-anion catalysis:} \left\{ \begin{array}{l} A \xrightarrow{k_A} \\ B \xrightarrow{k_B} \end{array} \right\} \text{Products}$$

$$\text{Contributions to two-anion catalysis:} \left\{ \begin{array}{l} C \xrightarrow{k_C} \\ D \xrightarrow{k_D} \\ E \xrightarrow{k_E} \end{array} \right\} \text{Products}$$

Let a, b, and c be the stoicheiometric (*i.e.*, the introduced) concentrations of HgX_2, RHgX, and MX respectively. Let $\bar{a}$, $\bar{b}$, and $\bar{c}$ be the concentrations, respectively, in which these substances survive when all the equilibria formulated above have been established. And let $\bar{d}$, $\bar{e}$, $\bar{f}$, and $\bar{g}$ be the concentrations of the complexes, HgX_3^-, HgX_4^{2-}, $RHgX_2^-$, and $RHgX_3^{2-}$, respectively, when all the equilibria are established.

Case 1. Consider first the case in which MX is in deficit: $c < a$. Then, because of our assumptions concerning the equilibria, $\bar{b} = b$ and $\bar{d} = c$. Hence the rate of the reaction of A will be $k_A\bar{b}\bar{d} = k_A bc$. Because of the equilibrium between A and B, the rate of the reaction of B will be $k_B(K_3/K_1)bc$. The sum of these rates is that of one-anion catalysis. It is easily seen that the rates of the reactions of C, D, and E, which compose two-anion catalysis, will be negligible in comparison with their respective rates in the case, next to be considered, in which two-anion catalysis becomes comparable in magnitude with one-anion catalysis. Since when we reduce c, two-anion catalysis fades out at first, we can safely assume that it makes no effective contribution to substitution rate in the present case. Hence the total rate, which is simply the exchange rate, k_0^{Hg}, is given by

$$k_0^{Hg} = \left(k_A + k_B \cdot \frac{K_3}{K_1} \right) bc = \kappa_1 bc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where κ_1 is our first omnibus constant, and is defined by this equation.

Case 2. Consider now the situation in which MX is in excess: $c > a$. Then, as before, $\bar{b} = b$; but now $\bar{c} = c - a$, and $\bar{d} = a$. Also $\bar{e} = K_2\bar{c}\bar{d} = K_2 a(c - a)$; and $\bar{f} = K_3\bar{b}\bar{c} = K_3 b(c - a)$. The rate of the reaction of A will now be $k_A\bar{b}\bar{d} = k_A ab$, and, as before, that of the reaction of B will be $(k_B/k_A)(K_3/K_1)$ times this. Hence, the contribution of one-anion catalysis to the rate will be $\{k_A + k_B(K_3/K_1)\}ab = \kappa_1 ab$ by (ii). The rate of the reaction of C will be $k_C\bar{b}\bar{e} = k_C K_2\, ab(c - a)$; the rate of the reaction of D will be $k_D\bar{d}\bar{f} = k_D K_3 ab(c - a)$; and the

rate of the reaction of E will be $(k_E/k_D)(K_4/K_1)$ times this. These three rates compose the contribution of two-anion catalysis to the total rate, which will be

$$k_0^{Hg} = \left\{\kappa_1 + \left(k_O K_2 + k_D K_3 + k_E \frac{K_3 K_4}{K_1}\right)(c - a)\right\}ab = \{\kappa_1 + \kappa_2(c - a)\}ab \quad . \quad \text{(iii)}$$

where κ_2 is our second omnibus constant, and is defined by this equation.

If $c \approx a$, so that $(c - a)$ becomes of the order of the error in our setting of the equilibrium (barred) concentrations—errors arising from the circumstance that the equilibrium constants, taken as large or small, are in reality neither infinite nor infinitesimal—then equations (ii) and (iii) will not hold. But the range of c so affected may well be small enough, or else the disturbances many be sufficiently self-compensatory, to allow them to pass unnoticed in experiments at spaced-out c values. Supposing this to be so, we can combine equations (ii) and (iii) at $c = a$, at which they give the same rate, $\kappa_1 ab = \kappa_1 bc$. Then, using the definition of $k_2^{(1)}$ given in Section 2 of Part IV,[1] *viz.*, $k_0^{Hg} = k_2^{(1)}ab$, we arrive at equation (i), already set down in Section 5 of this paper.

The argument of Section 5 above has benefitted from discussions with Professor R. S. Nyholm. A Ramsay Fellowship held by one of us (H. C. V.) is gratefully acknowledged.

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[*Received, September 20th*, 1960.]

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229. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part V.*[1] *Rubidium Hydrogen Di-o-nitrobenzoate and Potassium Hydrogen Di-p-nitrobenzoate.*

By H. N. Shrivastava and J. C. Speakman.

Acid salts, MHX_2, of monocarboxylic acids, HX, can be divided into two classes: in *A*, the two acidic radicals are equivalent and joined by a hydrogen bond that is crystallographically symmetrical; in *B*, the acidic radicals are non-equivalent, and X^- and HX can be distinguished in the crystal structure. The infrared spectra of type *B* compounds are essentially a superposition of those of the free acid and the neutral salt, whilst the spectra of type *A* are anomalous. On the basis of their dissimilar spectra, it had been suggested that the acid potassium salts of *o*- and *p*-nitrobenzoic acid belong to types *A* and *B* respectively. A structural study with *X*-rays has now confirmed that the *o*-nitro-salt, examined in the form of its rubidium isomorph, has a structure of type *A*, with a short hydrogen bond. Overcrowding in the acid radical is avoided by twisting of the carboxyl group well out of the plane of the benzenoid ring and nitro-group. The structure of potassium hydrogen di-*p*-nitrobenzoate has also been determined, and has been more fully refined by partial three-dimensional analysis. This structure is confirmed as being of type *B*. It embodies a very short hydrogen bond ($O \cdots O = 2{\cdot}49$ Å), of a non-symmetrical kind. Significant differences between these two representative structures are described.

The crystalline acid salts of monocarboxylic acids (HX) studied in this laboratory fall into two structural types, *A* and *B*. (These types correspond in part‡ to the classification of a wider range of hydrogen-bonded compounds described by Blinc, Hadži, and Novak.[2]) In type *B*, of which ammonium hydrogen disalicylate hydrate is an example,[1] the acidic radicals in the formula, M^+X^-,HX, are crystallographically distinct; one of them can be recognised as the anion and the other as in the neutral molecule. In type *A*, of which potassium hydrogen bisphenylacetate[3] is an example and to which most of the acid salts belong, X^- and HX are crystallographically equivalent; they are related to one another

[1] Part IV, Downie and Speakman, *J.*, 1954, 787.
[2] Blinc, Hadži, and Novak, *Z. Elektrochem.*, 1960, **64**, 567.
[3] Part I, Speakman, *J.*, 1949, 3357.

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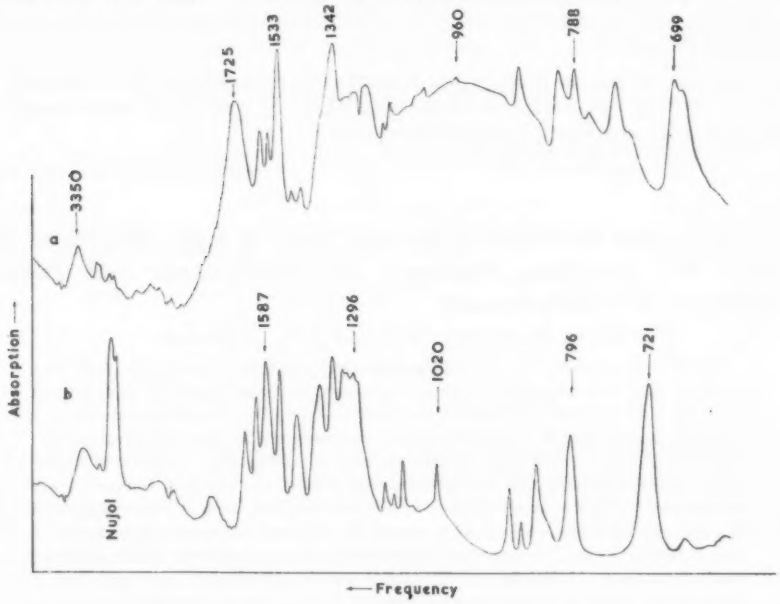
by a symmetry element, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. Such a bond, like those in the alkali bifluorides and a few other remarkable compounds, but unlike nearly all other hydrogen bonds, is therefore symmetrical—or, at least, formally so.

The infrared spectra of these acid salts have been studied particularly by Hadži and his co-workers,[4] who noticed that the two types give different types of spectrum. With type *B*, the spectrum approximates to a simple superposition of those of the free acid and neutral salt, each taken separately. With type *A* anomalous spectra are found: the OH stretching frequency, even if it be recognisable at all, is shifted to a much lower value than

FIG. 1. *Infrared spectra of* (a) *potassium hydrogen di-o-nitrobenzoate in* KCl *disc, and of* (b) *potassium hydrogen di-p-nitrobenzoate in Nujol mull. The frequencies marked are in cm.*$^{-1}$.



its normal one of ~3500 cm.$^{-1}$; and there is a wide plateau of high absorption spreading for several hundred wave-numbers on either side of its culmination somewhere in the region 700—1000 cm.$^{-1}$. These anomalies are presumed to be connected in some way with the symmetrical hydrogen bonding.[5]

Acid potassium salts of *o*- and *p*-nitrobenzoic acid would have been expected to have similar infrared spectra. In fact they differ greatly, as can be seen in Fig. 1, and in the sense described above; and on this basis Hadži[6] predicted that their crystal structures would differ, the *ortho*-compound belonging to type *A*, the *para*-compound to type *B*. The *X*-ray analyses recorded in this paper confirm his prediction. The structure of the acid *o*-nitrobenzoate has for convenience been studied in the isomorphous rubidium salt. This analysis has been pursued only far enough to prove the structure to be of the symmetrical type (*A*). The structure of potassium hydrogen di-*p*-nitrobenzoate turned out to be a new variant of type *B*, and this analysis has been highly refined by two-, and partial three-, dimensional methods.

[4] *E.g.*, Hadži and Novak, *Nuovo cim.*, 1955, **2**, Suppl. [x], 715; "Infrared Spectra of, and Hydrogen Bonding in, Some Acid Salts of Carboxylic Acids," University of Ljubljana, 1960.
[5] *E.g.*, Albert and Badger, *J. Chem. Phys.*, 1958, **29**, 1193.
[6] Hadži, personal communication, 1958.

Experimental

Acid salts of the nitrobenzoic acids were first described by Farmer.[7] In general they are easily prepared by dissolving 1 mole of the acid and ½ equivalent of alkali, or alkaline carbonate, in a little hot aqueous alcohol, and allowing the solution to cool, or evaporate. They may be recrystallised from the same medium; though, since these acid salts decompose into free acid and neutral salt in solution, care is needed lest the former crystallise out and be mistaken for the acid salt. There is no difficulty in preparing isomorphous potassium and rubidium acid *o*-nitrobenzoates. Both were studied with *X*-rays so far as to demonstrate their isomorphism; but structure analysis was mainly restricted to the rubidium compound, as the heavier atom led to a readier solution of the phase problem and as an accurate determination of atomic co-ordinates was not intended. From *p*-nitrobenzoic acid an acid potassium salt is easily made. But the failure of repeated attempts to prepare isomorphous ammonium, rubidium, or thallous salts suggested that the structure obtaining in the potassium compound depends critically upon the radius of the cation.

Crystal data were derived from single-crystal rotation, oscillation, and moving-film photographs; intensities were determined visually from multiple-film Weissenberg exposures; copper $K\alpha$-radiation was used throughout. For calculating structure factors, F_c, standard [8] atomic-scattering functions were used.

Rubidium Hydrogen Di-*o*-nitrobenzoate

Crystal Data and Structure Analysis.—$RbH(C_7H_4NO_4)_2$, $M = 418{\cdot}7$, triclinic pinakoidal $a = 13{\cdot}8_0$, $b = 4{\cdot}74$, $c = 6{\cdot}08$ Å, $\alpha = 100{\cdot}5°$, $\beta = 99{\cdot}4°$, $\gamma = 95{\cdot}0°$, $U = 383{\cdot}0$ Å^3, $D_m = 1{\cdot}82$ (by flotation in $CHBr_3$–CCl_4), $Z = 1$, $D_c = 1{\cdot}815$, $F(000) = 208$, absorption coefficient for *X*-rays 53 cm.$^{-1}$.

An unsophisticated application of the Wilson-ratio and $N(z)$ tests to the $h0l$-intensity data suggested that the space group was $P1$. This erroneous conclusion was due to the effect of the heavy atom. When proper allowance was made for it, by Sim,[9] centrosymmetry was indicated, requiring the space group to be $P\bar{1}$. The stoicheiometric molecule, of the above formula, must therefore possess a centre of symmetry, and the rubidium and acidic hydrogen atoms must be in special positions of symmetry $\bar{1}$. This at once implies that the structure belongs to class *A*.

Confirmation followed from a structure analysis based on the $h0l$- and $hk0$-reflexions: an electron-density projection, computed first with all signs positive, revealed the approximate structure; the atomic positions were then used in calculations of F_c-values, which showed that a few terms should have negative signs. Inclusion of these negative terms led to adequate, final electron-density maps, one of which is reproduced in Fig. 2. Differentiation between carboxyl and nitro-groups was possible because of differences in the heights of the appropriate peaks for carbon and nitrogen atoms. Absorption corrections were applied to the $h0l$-data by a version of Albrecht's method adapted for ready calculation on the DEUCE computer. A uniform, isotropic value of 3·0 Å^2 was used for the Debye temperature factor, *B*. Calculated structure factors, and observed structure amplitudes ($|F_o|$) are listed in Table 1. For 130 observed reflexions in the $h0l$-zone, *R* is 18·8%; for 122 in $hk0$ it is 17·8%. Fractional co-ordinates are given in Table 2, where are also shown co-ordinates, in Å, with respect to orthogonal axes, *X'* being parallel to *x*, *Y'* perpendicular to *x* in the *xy*-plane, and *Z'* perpendicular to *X'* and *Y'*. In this Table—as elsewhere in this paper and in Part VI—co-ordinates are often given to more figures than are significant; this has been done to avoid the discrepancies in derived quantities that can otherwise arise from rounding-off. The numbering of atoms is given in Fig. 2.

The hydrogen bond must lie acrosss the centre of inversion at 00½ between two carboxylic oxygen atoms, O(2) and O(2'). The co-ordinates lead to an O · · · O distance of 2·43 Å, the possible error of which may be informally assessed at not less than ±0·06 Å. That the structure is of type *A* is verified. A detailed consideration of the spectrum has suggested [9] that the hydrogen bond may be of the " single symmetric minimum " kind. The structure analysis is not inconsistent with this suggestion.

[7] Farmer, *J.*, 1903, **83**, 1440.
[8] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[9] Sim, *Acta Cryst.*, 1958, **11**, 123.

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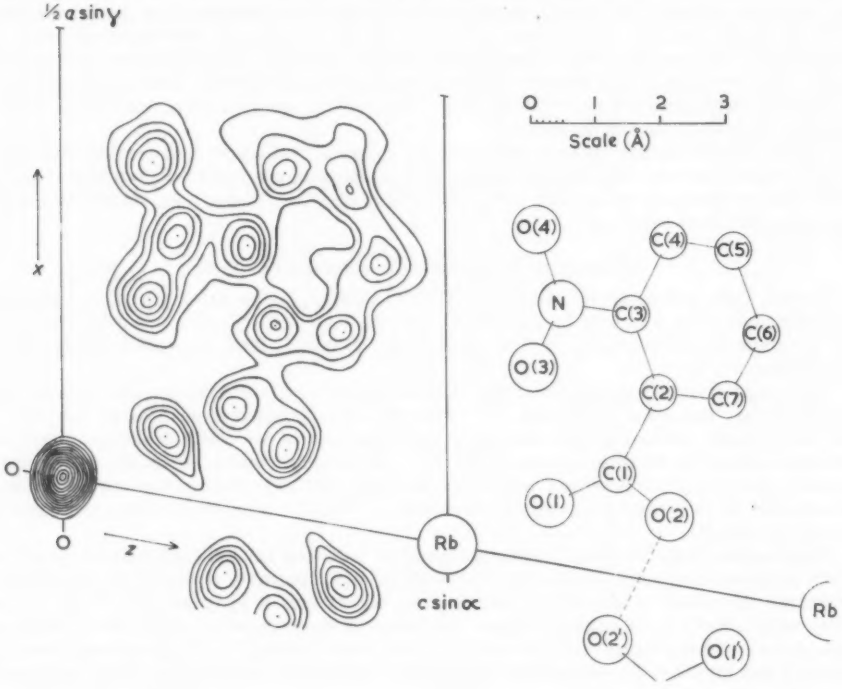
In the aromatic acid salts of type *A* examined hitherto, the metallic cations lie on two-fold symmetry axes; in this *o*-nitrobenzoate there is the minor difference that they lie at centres of symmetry. Were the nitrobenzoate residue planar, oxygen atoms 1 and 3 of the carboxyl and nitro-groups respectively would be separated by only about 1·5 Å. This severe over-

FIG. 2. *Rubidium hydrogen di-o-nitrobenzoate: electron-density projected along* b*-axis, with its interpretation and numbering of atoms. (Contour-line scale: for lighter atoms, intervals of* 2 *electrons* Å^{-2}, *starting from* 2; *for rubidium atom, intervals of* 5, *starting at* 5.)



crowding is relieved—and the distance increased to about 2·9 Å—by the carboxyl group's twisting through some 70° out of the plane of the benzene ring. The nitro-group is approximately in the plane. The Rb · · · O distances lie within the range 2·85—2·95 Å.

POTASSIUM HYDROGEN DI-*p*-NITROBENZOATE

Crystal Data. $KH(C_7H_4NO_4)_2$, $M = 372{\cdot}3$, triclinic pinakoidal, $a = 17{\cdot}20$, $b = 4{\cdot}05$, $c = 11{\cdot}44$ Å, $\alpha = 93{\cdot}8°$, $\beta = 104{\cdot}1°$, $\gamma = 90{\cdot}5°$, $U = 771{\cdot}3$ Å^3, $D_m = 1{\cdot}65$ (by flotation), $Z = 2$, $D_c = 1{\cdot}606$, $F(000) = 380$, absorption coefficient for *X*-rays $= 35{\cdot}4$ cm.$^{-1}$.

Statistical examination of the *h*0*l*-zone intensities suggested centro-symmetry and implied that the space group was $P\bar{1}$, and this was borne out by the subsequent analysis. No molecular symmetry is required. The crystals consist of thin laths, elongated in the *b*-direction and with the faces (100) most prominently developed.

Determination and Refinement of the Structure.—The structure was first determined as it appears projected along the short *b*-axis. Some 235 *h*0*l*-reflexions were originally recorded. At a late stage in the refinement an additional 90 weak reflexions were observed on films that had received a long exposure. The total of 325 is 70% of those accessible. The crystal used had a cross-section of 0·05 × 0·08 mm.^{2}, and absorption corrections were not applied.

The shortness of the *b*-axis implied that a well-resolved projection was obtainable, and that the nitrobenzoate residues were not tilted far out of the plane of projection. Nevertheless the

TABLE 1. *Observed structure amplitudes and calculated structure factors for rubidium hydrogen di-o-nitrobenzoate.*

h	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c
	A00			A02			A04			A06			A10			A30	
2	2·1	−5·5	$\bar{13}$	4·4	3·9	$\bar{14}$	13·0	20·6	$\bar{4}$	7·0	7·5	10	22·7	9·1	$\bar{4}$	11·5	3·6
3	48·6	57·5	$\bar{12}$	11·3	17·3	$\bar{13}$	11·1	16·2	$\bar{3}$	10·9	8·2	11	34·8	25·0	$\bar{3}$	9·6	5·3
4	15·8	17·5	$\bar{11}$	17·6	17·5	$\bar{10}$	5·6	9·5	$\bar{2}$	10·4	7·1	13	9·6	5·4	$\bar{2}$	9·9	12·1
5	22·1	24·6	$\bar{10}$	17·2	15·0	$\bar{8}$	18·7	24·2	$\bar{1}$	9·4	8·1	14	11·5	12·5	$\bar{1}$	19·6	16·1
6	3·2	−3·7	$\bar{9}$	25·8	28·3	$\bar{7}$	14·9	12·1	1	10·5	6·7				0	31·8	27·8
7	2·5	−3·9	$\bar{8}$	6·6	9·3	$\bar{6}$	14·5	12·3	2	8·4	5·6		A20		1	16·5	16·9
8	10·1	15·3	$\bar{7}$	23·6	30·5	$\bar{5}$	29·4	34·6	3	16·0	9·3	$\bar{14}$	8·1	11·2	2	18·0	18·5
9	16·3	11·5	$\bar{6}$	56·5	60·8	$\bar{4}$	28·8	33·7	4	17·0	15·1	$\bar{13}$	15·6	15·4	3	21·1	24·0
10	31·7	32·0	$\bar{5}$	14·1	13·2	$\bar{3}$	26·7	27·4	6	7·1	3·2	$\bar{12}$	8·1	5·1	4	19·9	18·7
11	5·5	10·7	$\bar{4}$	7·1	7·7	$\bar{2}$	7·5	7·0	7	10·4	14·1	$\bar{11}$	8·7	10·9	5	22·7	27·3
13	19·9	23·7	$\bar{3}$	30·3	25·2	$\bar{1}$	24·9	22·2				$\bar{10}$	12·4	16·9	6	18·0	14·5
14	9·6	15·8	$\bar{2}$	50·2	46·9	0	41·6	37·6		A07		9	12·7	15·6	7	8·0	4·6
16	6·5	6·2	$\bar{1}$	46·6	42·7	1	8·6	8·7	$\bar{8}$	8·7	11·1	8	8·4	6·2	8	14·0	14·6
			1	42·1	32·7	2	14·0	9·2	$\bar{6}$	7·5	6·1	7	7·1	−0·8			
	A01		2	34·0	31·0	3	14·5	13·0	$\bar{4}$	7·7	7·1	6	25·8	30·6		A40	
$\bar{13}$	14·3	20·3	3	7·4	6·7	4	8·4	5·1	$\bar{3}$	8·5	9·5	5	29·8	29·0	$\bar{10}$	8·7	13·2
$\bar{11}$	14·1	11·8	4	36·5	28·8	5	13·4	11·5	$\bar{2}$	9·4	7·9	4	9·0	13·4	$\bar{9}$	11·5	12·8
$\bar{9}$	22·1	24·2	6	3·7	4·9				$\bar{1}$	10·7	8·4	3	28·9	36·0	$\bar{8}$	11·7	14·1
$\bar{8}$	19·9	19·9	7	36·6	28·8		A05		0	13·6	11·1	2	21·8	19·0	7	9·6	9·1
$\bar{7}$	26·3	33·1	8	26·3	18·6	$\bar{12}$	13·8	16·5	1	9·7	8·0	1	23·3	27·2	$\bar{6}$	13·9	14·7
$\bar{6}$	48·5	45·6	9	25·9	13·8	$\bar{11}$	11·5	15·1	2	7·7	5·8	0	61·5	51·8	$\bar{5}$	15·2	15·1
$\bar{5}$	39·1	44·0	10	22·6	11·8	$\bar{10}$	7·0	13·5				1	23·0	21·0	$\bar{4}$	8·1	6·7
$\bar{4}$	51·9	54·7	11	17·1	12·0	$\bar{9}$	16·1	18·2		A10		2	11·2	9·1	$\bar{3}$	11·8	13·2
$\bar{3}$	32·1	31·7	12	9·4	12·1	$\bar{8}$	16·1	17·5	14	9·0	10·2	3	27·0	25·7	$\bar{2}$	9·3	4·8
$\bar{2}$	48·1	49·8				$\bar{7}$	5·7	10·2	$\bar{13}$	15·6	13·2	4	39·5	37·0	$\bar{1}$	8·0	5·8
$\bar{1}$	29·9	29·8		A03		$\bar{6}$	7·3	9·7	$\bar{12}$	13·0	12·7	5	23·9	19·8	0	21·7	22·3
0	24·4	−20·1	$\bar{13}$	17·1	21·5	$\bar{5}$	17·5	17·9	$\bar{11}$	12·4	13·3	7	7·5	8·2	1	16·7	9·8
1	11·6	9·3	$\bar{12}$	19 0	25·5	$\bar{4}$	15·9	15·9	$\bar{10}$	18·9	20·5	8	15·8	13·9	2	8·1	3·6
2	28·4	28·4	$\bar{11}$	12·1	22·3	$\bar{3}$	15·4	14·0	$\bar{9}$	32·0	22·9	9	8·4	8·7	3	10·9	12·2
3	29·8	25·5	$\bar{10}$	20·0	26·0	$\bar{2}$	19·4	17·5	$\bar{8}$	23·9	24·8	10	8·0	8·7	4	12·1	11·8
4	19·4	22·1	$\bar{9}$	13·5	18·4	$\bar{1}$	18·2	16·5	$\bar{7}$	24·3	28·6	11	10·5	8·5	5	9·6	10·1
5	25·5	26·7	$\bar{8}$	25·7	31·4	0	13·4	12·8	$\bar{6}$	22·4	18·8	12	12·4	10·4	7	9·3	7·9
6	29·2	30·5	$\bar{7}$	24·4	22·8	1	17·0	7·9	$\bar{5}$	12·4	17·6	13	14·9	13·6	8	8·7	10·2
7	22·0	23·4	$\bar{6}$	14·3	14·6	2	18·5	12·0	$\bar{4}$	18·7	12·6	14	14·0	12·5	9	6·2	7·2
8	19·6	19·3	$\bar{5}$	16·0	15·2	3	10·8	8·6	$\bar{3}$	19·3	16·4				10	8·1	7·9
9	16·2	13·2	$\bar{4}$	13·0	12·3	5	18·0	10·5	$\bar{2}$	19·6	21·8		A30		11	6·5	5·2
10	4·4	9·9	$\bar{3}$	30·2	28·6	6	16·7	9·3	$\bar{1}$	4·3	−11·6	$\bar{14}$	7·1	8·3			
11	10·1	11·0	$\bar{2}$	9·5	6·2	8	9·6	6·5	0	25·2	39·7	$\bar{13}$	8·1	8·9		A50	
12	10·8	10·4	$\bar{1}$	14·5	14·3	9	5·7	8·7	1	76·9	68·0	$\bar{12}$	7·8	8·1	7	9·3	10·1
13	9·5	10·6	1	42·0	38·4				2	26·4	25·6	$\bar{11}$	17·1	18·0	$\bar{6}$	10·8	7·3
15	6·6	4·7	2	33·5	27·2		A06		3	46·7	49·2	$\bar{10}$	18·3	19·3	$\bar{2}$	8·7	9·4
			3	31·1	23·7	$\bar{10}$	8·8	15·3	4	31·1	36·0	9	16·7	15·7	$\bar{1}$	8·4	2·9
	A02		4	28·1	22·0	$\bar{9}$	10·6	17·3	5	24·5	24·9	$\bar{8}$	16·5	18·2	1	10·2	8·8
			5	25·0	21·6	$\bar{7}$	17·8	23·9	6	21·8	24·3	$\bar{7}$	8·0	5·0	2	10·2	7·5
$\bar{16}$	7·1	12·9	6	23·3	22·0	$\bar{6}$	30·8	32·8	7	8·7	8·2	$\bar{6}$	5·6	5·9	3	12·4	14·2
$\bar{15}$	8·4	13·0	7	13·8	9·2	$\bar{5}$	6·9	2·9	8	21·8	21·1	$\bar{5}$	13·4	17·2	4	10·5	7·9
															5	6·2	6·2

TABLE 2. *Rubidium hydrogen di-o-nitrobenzoate, fractional co-ordinates* (x, y, *and* z), *and orthogonal co-ordinates in* Å (X′ *parallel to* x, Y′ *perpendicular to* x *in the* xy*-plane, and* Z′ *perpendicular to* X′ *and* Y′). *Origin at centre of inversion.*

Atom	*x*	*y*	*z*	*X′*	*Y′*	*Z′*
Rb	0·0000	0·0000	0·0000	0·000	0·000	0·000
O(1)	0·0680	0·5870	0·2730	0·425	2·444	1·604
O(2)	0·0780	0·9250	0·5800	0·118	3·672	3·409
O(3)	0·2190	1·0270	0·2320	2·368	4·571	1·364
O(4)	0·3730	0·9870	0·2410	4·500	4·372	1·416
N	0·2916	0·9450	0·3000	3·336	4·103	1·763
C(1)	0·1127	0·7400	0·4470	0·806	2·958	2·627
C(2)	0·2150	0·6790	0·5530	2·137	2·543	3·250
C(3)	0·2950	0·7870	0·4800	3·269	3·141	2·821
C(4)	0·3850	0·7320	0·5810	4·434	2·760	3·415
C(5)	0·3900	0·5800	0·7420	4·406	1·849	4·361
C(6)	0·3050	0·4670	0·8200	3·202	1·222	4·819
C(7)	0·2200	0·5200	0·7200	2·106	1·592	4·232

solution of the phase problem proved difficult. The *p*-nitrobenzoate group has high pseudo-symmetry (*mmm*), so that its vector-set includes prominent peaks due to the coincidence—or near-coincidence—of several interatomic vectors. Against a background of two such independent sets, vector-peaks involving potassium atoms are less salient than normally. However,

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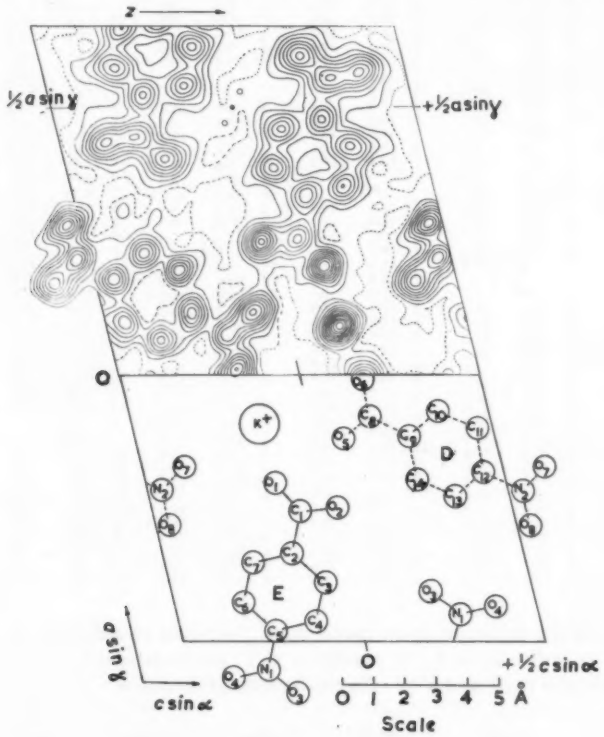
the failure to prepare crystals in which the potassium was isomorphously replaced made it necessary to solve the structure by an intensive study of the Patterson projection along [*b*].

For this purpose the projection was moderately sharpened by the function, $\{\hat{f}\exp(\sin^2\theta/\lambda^2)\}^{-2}$, in which $\hat{f}$ is an averaged unitary atomic-scattering function and the other symbols have their usual meanings. Previous experience had suggested that such a structure might be elucidated *via* the Buerger minimum function [10] when the Patterson map was superposed upon itself with

FIG. 3. *Potassium hydrogen di-p-nitrobenzoate: electron-density projected along* b*-axis, with its interpretation and numbering of atoms. (Contour-line scale: intervals of one electron* Å^{-2} *with zero-line broken, except for potassium atom, around which only the even contours are shown beyond* 2.)



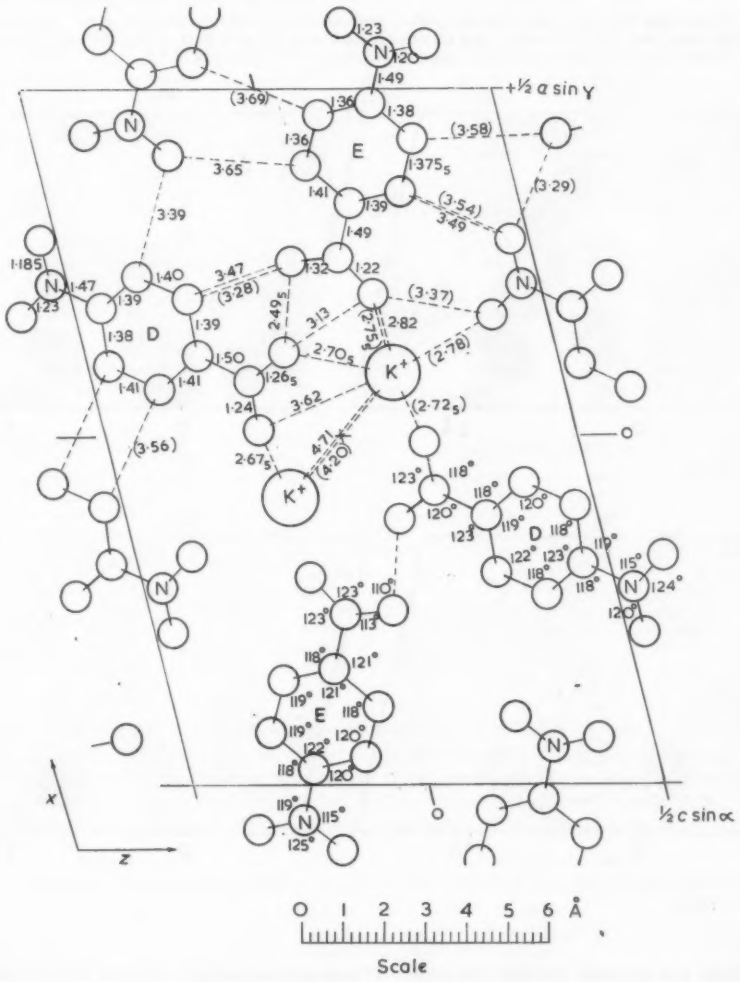
its origin on the peak corresponding to the K · · · K vector. This procedure was followed for several prominent peaks that might so correspond; but what was in fact the correct structure was not recognised in this way until it had also been indicated by another approach, which is described in the next paragraph.

The weighted vector-diagram for a single *p*-nitrobenzoate residue was drawn, to scale, on tracing paper. It includes a high-weight vector, about 6·7 Å from its origin, due to the pair of long O · · · O separations. It was placed with its origin on that of the sharpened Patterson map, and rotated into all the positions in turn where this O · · · O vector coincided with a Patterson peak. Each of the 12 positions was given a figure-of-merit based on the number and weights of any other coincidences. Three orientations were indicated as most probable. Next the Patterson map was searched for centre-to-centre vector-peaks between pairs of acid radicals related by the centre of symmetry. On each of the possible peaks the vector-diagram was placed, in each of its three most probable orientations; and it thus became possible to reject all

[10] Buerger, " Vector Space," Wiley, New York, 1959.

but two peaks and two orientations. These corresponded to the two independent nitrobenzoate residues. Thus the structure was revealed, so far as the acidic radicals were concerned, and the minimum function could be interpreted. The preliminary structure showed an agreement (R) of 33% between $|F_o|$ and $|F_c|$ computed with a Debye factor (B) of 3·0 Å^2, and it served as the starting point for refinement.

FIG. 4. *Potassium hydrogen di-p-nitrobenzoate: projection of the structure along the* b*-axis, showing intramolecular dimensions and the more important intermolecular contacts (in* Å).

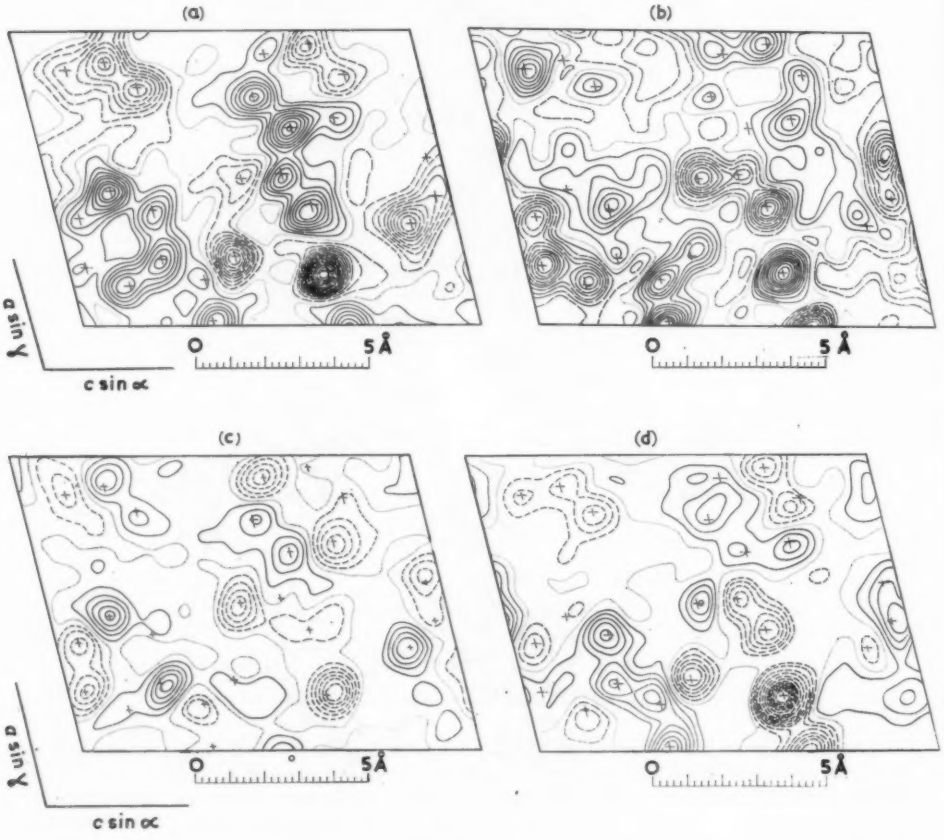


Two further cycles of electron-density syntheses reduced R to 19·0%; thereafter three cycles of "difference syntheses," with B now allowed to vary, reduced it to 13·0%. During the latter phase, the additional 90 reflexions were introduced; allowance for unobserved reflexions was made by giving them a structure amplitude equal to half the minimum locally observable; and the hydrogen atoms attached to carbon were included in F_c-calculations. A final cycle brought R to 11·5% for the original 235 terms, and to 14·0% for the 325. The map

in Fig. 3 shows the last electron-density synthesis, in which only the 235 terms were used. It is interpreted in the lower part of the diagram, where the numbering of atoms is also shown. Fig. 4 covers a more extensive region of the same projection. In the initial stages of refinement, no distinction was made between carbon and nitrogen atoms, so as not to prejudge the question of the identities of carboxyl and nitro-groups. The question could soon be answered, in the sense of Fig. 3, because the electron-density peaks for nitrogen were higher.

With well-established—though not final—values for x- and z-, y-co-ordinates were sought by

FIG. 5. *Potassium hydrogen di-*p*-nitrobenzoate: generalised projections along* b*-axis.* (a) cosine *part, and* (b) sine *part, with* $h1l$*-data; and* (c) cosine *part, and* (d) sine *part with* $h2l$*-data. (Zero-contour line dotted, negative contours broken: lines at intervals of one electron* Å^{-2}.)



way of some 240 $h1l$- and 180 $h2l$-reflexions. (These are respectively 52 and 55% of the totals accessible in these reciprocal-lattice nets.) By trial a set of y-co-ordinates was found, and they were refined by six cycles of generalised projections, first for the $h1l$-terms, then for the $h2l$-terms, both sine and cosine components being evaluated in each case. Maps representing these generalised projections, in their final forms, are shown in Fig. 5.

In a last phase, a partial three-dimensional least-squares refinement was effected with the available reflexions (nearly 750) of types $h0l$, $h1l$, and $h2l$, provision being made for anisotropic thermal parameters. The weighting system was that described in Part VI. In the last two of

three cycles of refinement, unobserved reflexions were included, at half the minimum value of $|F_o|$ locally observable, for all those reflexions (some 250) for which $|F_c|$ exceeded this minimum. The value of R was thus reduced to 10·4% for all observed reflexions. Final positional

TABLE 3. *Potassium hydrogen di-*p*-nitrobenzoate, fractional co-ordinates* (x, y, *and* z), *orthogonal co-ordinates* (*in* Å, *with* Y′ *parallel to* y, Z′ *perpendicular to* y *in the* yz*-plane, and* X′ *perpendicular to* Y′ *and* Z′), *and thermal parameters* (B) *parallel to each principal axis. Origin at a centre of inversion.*

Atom	*x*	*y*	*z*	*X′*	*Y′*	*Z′*	*B*||*x*	*B*||*y*	*B*||*z*
K	0·09075	0·34914	0·14252	1·5140	1·2932	1·2475	4·5	2·8	5·1
O(1)	0·20249	−0·13449	0·14498	3·3782	−0·6851	0·8086	4·2	1·9	6·4
O(2)	0·24954	−0·29750	−0·01429	4·1632	−1·2339	−1·2062	4·7	5·3	3·6
O(3)	0·59816	0·57259	0·21544	9·9794	2·0630	−0·0411	6·6	10·0	8·4
O(4)	0·56426	0·69715	0·38155	9·4138	2·4489	1·9968	7·1	9·3	7·9
O(5)	0·11834	0·39474	−0·07826	1·9745	1·6382	−1·3880	4·9	4·8	4·8
O(6)	0·00551	0·14065	−0·17499	0·0919	0·6993	−2·0206	4·9	2·4	7·3
O(7)	0·17253	−0·52368	−0·61787	2·8784	−1·6872	−7·7746	7·4	6·4	5·5
O(8)	0·28551	−0·28577	−0·53461	4·7633	−0·8039	−7·2964	6·5	6·9	7·3
N(1)	0·55283	0·55892	0·28326	9·2231	1·9643	0·9226	5·5	9·1	5·8
N(2)	0·21729	−0·35078	−0·53672	3·6356	−1·0548	−7·0379	6·0	4·7	5·2
C(1)	0·25553	−0·13531	0·09116	4·2631	−0·6567	−0·0275	5·3	1·6	5·5
C(2)	0·33435	0·04238	0·13938	5·5781	0·0144	0·1934	4·2	1·5	5·4
C(3)	0·38818	0·08298	0·06542	6·4762	0·2255	−0·8759	4·2	1·8	5·6
C(4)	0·46070	0·23061	0·11710	7·6860	0·7733	−0·5891	4·2	3·5	6·7
C(5)	0·47530	0·37792	0·23075	7·9296	1·2827	0·6472	4·4	4·5	6·1
C(6)	0·42284	0·34705	0·30373	7·0544	1·1116	1·6996	4·9	4·8	5·0
C(7)	0·34986	0·18937	0·25634	5·8368	0·5200	1·4637	5·0	3·0	5·1
C(8)	0·07646	0·22000	−0·16724	1·2756	1·0036	−2·2287	3·6	4·1	5·8
C(9)	0·11485	0·07500	−0·26249	1·9161	0·4814	−3·4765	5·0	1·1	4·0
C(10)	0·06697	−0·11652	−0·36086	1·1172	−0·2133	−4·3994	4·0	4·1	5·0
C(11)	0·10039	−0·25701	−0·45330	1·6748	−0·7186	−5·5943	5·1	1·3	5·1
C(12)	0·18103	−0·19924	−0·44415	3·0202	−0·5043	−5·8270	5·9	2·4	4·0
C(13)	0·23040	−0·01721	−0·34710	3·8438	0·1526	−4·9255	4·3	2·9	5·0
C(14)	0·19601	0·11568	−0·25640	3·2701	0·6286	−3·7463	3·3	3·5	4·2

	x	*y*	*z*		*x*	*y*	*z*
H of C(3) ...	0·375	−0·021	−0·026	H of C(10) ...	0·007	−0·151	−0·362
H of C(4) ...	0·504	0·250	0·068	H of C(11) ...	0·063	−0·123	−0·537
H of C(6) ...	0·441	0·442	0·402	H of C(13) ...	0·292	0·015	−0·345
H of C(7) ...	0·310	0·179	0·308	H of C(14) ...	0·223	0·251	−0·176

parameters are listed in Table 3, which also includes co-ordinates, in Å, with respect to orthogonal axes chosen with Y' parallel to y, Z' perpendicular to y in the yz-plane, and X' perpendicular to both Y' and Z', and anisotropic B-factors parallel to each of the principal axes. (Individual values of $B||y$ are of qualitative, rather than quantitative, significance.) During the final least-squares cycle, hydrogen atoms were included in the calculation of F_c, though

TABLE 4. *Standard deviations* (Å) *in atomic positions* (r) *and bond-lengths.*

Atom	$\sigma(r)$	Bond	σ
K^+	0·0053	$K^+ \cdots O$ (carboxyl)	0·015
O (carboxyl)	0·0144	$K^+ \cdots O$ (nitro)	0·019
O (nitro)	0·018	O ··· O (hydrogen bond)	0·020
N	0·020	N–O	0·027
C	0·022	C–O	0·026
		C–C	0·031

their parameters were not refined. Their y-co-ordinates, shown in Table 3, were derived geometrically from the already assigned x- and z-co-ordinates, with the assumption that the hydrogen atoms must lie in the (mean) planes of their respective benzenoid rings. For one

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TABLE 5. *Observed structure amplitudes and calculated structure factors for potassium hydrogen di-p-nitrobenzoate.* (*Terms marked with an asterisk were not observed because of their low values of* sin θ.)

h	½F_o	½F_c
	h00	
2	1·9	−1·6
3	21·9	−22·8
4	4·9	−4·9
5	1·8	1·3
6	25·1	−27·1
7	8·2	−8·1
8	4·5	−4·6
9	15·6	14·7
10	11·9	10·8
11	14·2	13·0
12	5·9	5·7
	h01	
19	3·3	−2·8
18	5·7	−5·7
17	4·3	−4·7
15	8·1	8·5
14	4·4	−4·4
13	7·1	7·1
12	6·2	6·1
11	1·5	1·8
10	5·5	−5·6
9	3·9	4·8
8	7·1	7·3
7	1·4	−2·1
6	8·8	−9·6
5	17·0	−18·8
4	2·4	2·1
3	1·9	2·0
2	1·3	−0·1
1	8·7	7·8
0	9·3	8·4
1	1·4	−2·1
2	16·2	17·7
3	14·6	16·4
4	10·4	−12·2
6	6·4	−6·6
7	11·7	−12·2
8	22·8	23·7
9	4·2	4·8
10	8·1	8·5
11	3·7	3·1
12	3·5	1·8
13	2·9	−2·9
14	3·4	−4·5
19	3·2	2·0
20	2·8	2·1
	h02	
20	2·8	−2·5
19	3·0	−2·8
17	2·8	−2·4
16	4·6	4·6
15	2·1	−2·6
13	3·4	3·3
11	2·7	−3·4
10	8·6	−8·0
9	15·5	−15·3
8	14·7	−14·4
7	1·6	1·5
6	5·7	−6·8
5	8·9	9·7
4	11·3	11·9
3	12·6	13·5
2	26·0	−27·1
1	28·2	29·6
0	11·4	−12·5
1	8·5	−10·0
2	26·3	−29·5
3	14·2	−14·1
4	4·9	6·3
5	18·9	−20·3
6	3·8	−4·1
7	3·9	3·5
8	23·5	23·4
12	3·3	−3·4
13	2·3	−1·9
14	5·4	−5·0
15	2·6	−2·2
16	1·5	−1·6
18	2·1	2·6
19	1·5	1·6
	h03	
21	1·3	−1·1
20	2·8	−1·9
19	2·8	−2·0
18	1·4	0·4
16	12·2	11·8
15	3·7	−3·7
13	1·7	−1·4
12	2·5	−2·0
11	5·8	−5·8
10	24·3	−24·5
9	12·4	−13·1
8	4·1	3·9
7	8·0	9·4
6	2·7	3·4
5	15·7	17·0
4	3·3	−3·3
3	10·4	−10·7
2	6·2	−5·7
1	4·5	−4·3
0	19·3	−20·4
1	32·4	−36·1
2	5·6	−5·6
4	9·6	9·4
5	5·9	5·6
6	6·5	−6·1
7	10·0	9·6
10	8·9	−8·6
11	9·8	−9·4
12	1·5	−1·5
13	2·8	−2·6
18	1·3	1·2
	h04	
20	1·1	1·3
17	5·8	5·4
16	2·1	3·0
13	1·4	−1·1
12	8·4	−8·4
11	10·4	−10·2
10	5·4	−5·6
9	5·8	−6·4
8	22·2	23·0
7	5·4	5·9
6	12·1	14·1
5	2·0	1·9
4	1·8	1·9
3	13·4	14·0
2	23·4	−23·7
1	23·9	−26·2
0	13·1	−13·1
1	7·2	−8·2
2	3·1	2·8
3	3·8	−3·8
4	8·0	8·4
5	5·8	7·1
7	4·4	4·4
9	1·9	−1·3
12	3·7	−3·4
13	5·0	−4·9
	h05	
20	1·1	1·1
19	5·2	4·4
18	3·9	3·0
17	2·5	2·7
15	4·1	4·2
13	4·8	−4·8
12	3·7	−4·2
11	4·0	−4·4
10	1·8	−0·9
9	5·3	4·4
8	10·8	10·9
7	3·5	4·1
6	11·2	11·5
5	21·1	21·3
4	10·4	10·2
3	10·8	−10·1
2	19·4	−19·3
1	7·2	−7·7
0	4·1	−3·3
1	11·6	11·9
2	19·8	19·6
3	10·8	11·3
4	1·9	1·5
6	1·8	−1·6
7	1·3	−2·1
8	5·4	−5·3
9	10·1	−9·8
11	2·4	2·0
12	9·2	8·1
13	4·6	5·0
	h06	
21	2·6	2·0
19	2·1	1·5
17	1·4	−1·8
16	4·9	−4·5
15	7·2	−6·8
14	4·1	4·4
13	7·3	7·4
12	8·8	8·6
11	3·2	3·7
9	9·6	8·9
8	3·0	3·2
7	2·6	3·1
6	9·1	−8·8
5	14·1	−14·0
4	2·7	1·9
3	6·5	5·7
2	3·2	3·1
1	3·2	−3·1
0	1·1	2·2
1	19·7	20·7
2	2·3	−3·0
3	8·5	8·5
4	10·1	10·8
5	7·2	7·4
6	4·3	−4·3
7	7·5	−7·4
8	5·3	−4·8
9	2·6	−1·9
10	1·5	2·4
11	1·5	−1·4
12	3·5	3·2
13	3·6	2·5
14	2·8	2·1
15	1·2	1·2
	h07	
20	1·6	1·5
18	4·6	−4·4
17	6·4	−5·4
16	3·6	−3·3
15	1·8	−1·5
14	1·9	−2·2
13	7·0	−7·8
12	5·3	5·4
11	15·4	14·9
10	9·1	8·6
9	1·4	2·1
8	3·9	−3·8
7	8·6	−8·1
6	4·4	−5·2
5	5·0	−5·1
4	3·1	−3·2
3	1·7	−1·6
2	1·9	−2·6
1	3·9	4·3
0	8·5	7·9
1	6·6	6·1
3	1·6	−2·0
5	3·3	−3·6
6	1·5	−1·7
7	2·3	−2·0
8	4·3	−4·3
9	6·1	6·4
	h08	
19	1·3	−1·2
18	4·2	−3·4
17	3·5	−3·1
16	3·0	−3·0
15	2·3	2·0
13	2·6	2·5
12	3·4	2·7
11	3·9	3·9
9	4·2	−4·5
8	8·9	−8·1
7	8·5	−9·5
6	9·7	−10·5
5	2·3	2·8
4	4·2	4·5
3	4·4	3·8
1	2·3	2·2
0	6·7	6·7
2	5·5	−6·3
3	6·7	−7·7
4	2·3	−2·0
9	4·3	4·2
	h09	
18	1·9	−1·7
17	1·5	−1·5
15	4·6	5·3
12	2·1	2·4
10	3·5	−3·5
9	5·4	−5·7
8	5·0	−4·1
6	4·0	−3·6
5	3·5	−3·9
4	7·9	8·3
3	2·9	3·3
1	3·6	−3·9
2	5·6	−5·5
3	3·4	−3·3
5	2·1	1·7
8	4·2	3·8
	h0,10	
17	2·6	1·8
16	4·5	4·1
15	1·8	1·1
12	1·5	1·6
11	3·3	−2·3
10	4·5	−4·8
9	5·1	−4·3
7	2·1	−3·4
6	8·5	8·7
5	2·6	−3·5
4	3·8	4·2
3	5·5	5·6
2	8·2	8·5
1	4·0	4·1
0	5·6	−5·8
1	7·5	−6·4
2	4·4	−4·4
3	1·8	−1·6
4	3·7	−4·4
6	3·0	2·6
7	3·7	3·2
8	3·8	2·9
10	2·6	−2·1
11	1·5	−1·5
	h0,11	
17	4·4	3·4
16	2·6	2·3
13	2·9	−2·3
12	1·9	−1·3
10	1·4	−1·7
8	3·6	2·6
7	4·7	4·2
1	2·6	2·5
0	2·1	2·2
1	1·5	0·4
2	4·8	−4·2
4	2·7	2·4
5	1·8	1·2
7	1·1	−0·4
	h0,12	
16	1·7	1·4
14	1·6	−1·5
13	3·8	−3·2
12	1·2	−1·1
8	4·7	3·8
7	6·7	6·2
5	1·4	0·8
3	1·4	−1·8
2	3·9	−3·6
1	4·8	−3·4
1	4·4	4·6
2	2·4	1·3
3	2·3	1·6
	h0,13	
13	1·8	−1·6
10	2·3	1·5
9	1·8	0·9
3	1·2	1·5
2	1·2	−1·5
1	1·9	−1·8
3	2·3	−1·4
0	2·7	2·3
1	1·8	1·4
	h0,14	
10	2·2	1·3
7	1·3	−0·9
6	2·1	−2·1
4	2·6	−1·7
	h10	
8	6·4	−6·6
7	7·5	−7·7
6	8·3	7·9
4	7·7	7·8
3	55·5	67·3
2	*	22·9
1	*	7·0
0	3·9	−3·6
1	*	12·6
2	7·9	−5·7
3	34·0	−31·5
4	11·6	11·3
5	10·3	10·4
6	24·7	22·6
7	9·4	−9·3
8	13·3	12·5
	h1$\bar{1}$	
11	8·0	9·2
10	9·9	−11·4
9	13·9	−12·9
8	14·7	−13·6
7	7·2	−6·7
4	10·4	11·3
3	23·6	22·4
2	47·1	42·9
1	3·9	−1·9
0	6·9	6·0
1	*	−35·3
2	50·6	−42·7
3	16·8	−14·6
4	25·2	−23·3
5	4·1	−2·2
6	11·3	11·5
8	8·5	8·1
9	7·9	7·8
10	6·4	6·0
14	6·9	−7·2
15	6·3	−6·7
	h11	
9	4·4	−4·8
8	4·1	−4·0
7	11·3	10·9
6	6·9	6·9
5	20·2	21·9
4	26·0	25·0
3	18·4	18·1
2	24·6	22·7
1	*	1·0
0	3·5	5·9
1	17·6	−14·7
2	4·4	−5·1
3	16·0	−15·1
4	4·2	5·4
5	35·8	34·0
6	11·8	13·2
7	12·6	12·2
11	7·1	−7·0
	h1$\bar{2}$	
6	14·5	−16·3
5	12·1	−12·3
3	9·7	9·1
2	17·5	19·1
1	76·2	−83·8
0	6·0	−4·2
1	17·7	17·3
2	24·5	23·9
3	13·9	−13·1
4	17·3	−18·3
5	5·9	−6·0
6	6·1	−6·0
8	6·3	−7·1
9	4·5	−3·9
13	8·3	6·8
14	10·0	−8·7
15	5·7	−5·1
16	6·5	−6·8
	h12	
10	4·4	5·1
9	5·8	−5·9
8	7·3	6·8
7	9·9	8·4
6	13·0	12·8
4	11·3	−12·0
3	5·9	−6·4
2	7·0	5·6
1	10·2	−10·4
0	5·2	−4·1
2	7·7	7·7
3	11·0	11·5
4	8·3	9·3
5	25·4	25·2
6	5·8	−5·4
8	6·6	−6·8
9	10·8	−10·7
	h1$\bar{3}$	
10	7·0	8·1
9	5·1	−7·4
8	5·6	7·4
6	7·2	−7·8
5	11·6	−11·6
4	21·3	−23·4
3	12·6	−13·1
1	12·9	13·8
0	5·2	4·3
1	15·4	14·3
2	17·8	18·4
3	5·4	5·9
4	6·1	6·1
5	5·0	−4·6
6	20·9	−20·8
7	24·0	−25·3
8	9·2	−8·5
10	7·6	7·2
13	15·5	14·1
	h13	
15	7·4	−7·0
10	8·4	8·5
8	12·6	12·7
6	16·9	−16·5
5	21·0	−19·8
4	15·2	−14·1
3	5·5	−5·9
2	13·4	−15·3
1	2·8	−1·4
0	2·8	−2·1
1	9·5	−9·2
2	3·3	1·9
3	14·7	14·4
4	15·1	13·8
6	5·8	−5·8
7	6·6	−6·3
10	8·4	−7·5
11	11·1	−10·6
	h1$\bar{4}$	
10	5·6	5·8
9	3·6	−1·5
8	3·3	2·8
7	7·8	8·7
6	8·3	10·2
5	2·8	−3·7
4	9·4	−9·4
3	7·0	−6·2
2	7·4	−8·1
1	5·1	−5·6
1	15·1	16·6
2	14·8	13·8
3	14·5	13·4
4	2·9	3·0
5	15·0	16·2
6	13·9	−15·0
7	4.9	−5·3

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TABLE 5. (*Continued.*)

h	$\frac{1}{4}F_o$	$\frac{1}{4}F$
	A1$\bar{1}$	
8	7·3	−8·7
9	3·7	−3·5
12	5·1	5·4
13	5·3	5·6
14	13·5	13·6
	A14	
$\bar{15}$	8·4	−8·9
$\bar{14}$	10·9	−11·7
$\bar{13}$	8·7	−8·5
$\bar{12}$	12·9	13·2
9	7·2	8·1
7	4·2	3·7
6	6·9	6·9
5	25·9	−26·5
4	32·6	−31·5
3	20·7	−20·9
2	3·4	2·7
1	13·8	14·8
0	7·2	−8·0
$\bar{1}$	18·2	19·2
2	3·9	4·0
3	11·6	−10·8
4	16·3	−15·7
5	7·2	−7·1
	A1$\bar{5}$	
7	8·2	8·7
6	5·6	6·1
5	9·0	−9·3
1	3·8	−4·9
2	13·0	11·8
3	15·1	17·9
4	9·7	9·7
5	11·1	10·5
6	4·0	4·4
7	9·7	−9·9
14	10·2	9·8
	A15	
$\bar{14}$	8·3	9·6
7	5·0	−4·9
6	9·3	−9·1
5	10·5	−11·0
3	7·5	8·4
2	7·9	7·2
1	10·6	11·1
1	9·1	8·8
2	3·2	3·9
3	4·3	−5·6
4	7·1	−6·8
5	14·8	−13·6
6	8·8	−7·7
	A1$\bar{6}$	
$\bar{4}$	12·3	12·8
2	10·5	−11·5
4	9·2	9·5
5	5·4	5·0
6	8·9	8·7
7	6·8	−8·2
12	5·3	−6·4

h	$\frac{1}{4}F_o$	$\frac{1}{4}F_c$
	A16	
$\bar{14}$	6·8	6·1
$\bar{13}$	8·2	7·5
$\bar{12}$	5·6	6·4
7	9·0	−9·4
3	8·4	8·4
2	16·3	17·7
0	4·3	4·4
1	5·6	5·2
2	6·9	6·8
3	8·9	−8·7
4	11·0	−11·0
7	9·2	8·6
9	9·0	8·3
	A17	
3	12·3	−12·3
4	15·4	−15·4
6	6·0	6·9
7	5·3	7·6
8	6·1	6·0
13	9·7	−9·4
14	10·2	−9·7
	A17	
$\bar{15}$	6·6	6·9
$\bar{14}$	6·8	6·5
8	5·4	−5·4
6	11·4	11·4
4	7·1	8·0
3	10·0	11·3
2	5·1	5·8
2	5·6	−6·0
3	5·1	−4·5
4	3·6	−4·1
6	10·4	9·5
	A1$\bar{8}$	
3	6·7	7·6
2	11·0	−11·2
9	6·6	7·3
12	6·8	−6·9
13	8·1	−9·6
	A18	
$\bar{15}$	6·7	5·6
8	10·6	−10·4
7	6·5	6·6
5	5·8	6·1
5	3·5	3·9
4	3·5	−3·6
3	3·5	−4·3
	A19	
$\bar{13}$	4·5	−4·6
$\bar{12}$	6·7	−7·5
7	11·1	10·8
3	7·4	−7·7
2	13·3	−12·0
1	13·1	−12·3

h	$\frac{1}{4}F_o$	$\frac{1}{4}F$
	A20	
5	6·1	6·6
6	6·4	6·7
7	5·5	4·3
6	11·4	12·2
3	10·1	−15·1
	A2$\bar{1}$	
7	6·5	6·5
6	7·1	6·2
5	3·0	4·0
4	14·7	−15·3
3	14·4	14·4
2	17·0	−15·7
1	*	−19·6
0	*	−9·6
1	*	−16·7
	A21	
$\bar{10}$	10·4	10·1
8	9·8	9·0
7	10·4	10·4
6	6·0	6·7
5	7·2	−6·7
4	7·1	−5·3
3	6·1	−3·5
2	9·9	−7·7
	A2$\bar{2}$	
$\bar{10}$	5·8	−7·5
9	4·3	−5·3
8	6·1	5·5
5	13·6	11·7
4	20·4	−20·3
3	14·3	13·8
1	12·0	−11·6
0	30·6	−26·0
1	24·1	−16·4
	A22	
$\bar{11}$	6·3	5·8
$\bar{10}$	4·3	5·2
7	15·3	−14·8
5	10·7	10·0
4	6·1	6·2
2	6·6	−6·6
	A2$\bar{3}$	
8	4·3	−5·7
7	6·5	−5·5
3	11·9	−12·8
2	12·6	11·6
1	6·4	5·6
0	16·1	15·8
1	*	10·6
	A23	
$\bar{13}$	10·4	10·1
$\bar{12}$	7·9	7·9
$\bar{11}$	8·9	8·7
8	8·9	−8·8
7	10·8	−10·8
6	5·2	−3·4
5	12·3	−11·3

h	$\frac{1}{4}F_o$	$\frac{1}{4}F_c$
	A23	
3	6·3	7·5
2	19·9	17·6
1	5·9	4·2
0	2·8	4·5
	A2$\bar{1}$	
3	5·8	−7·0
2	31·9	33·4
1	20·7	22·3
0	*	1·9
1	*	−8·7
2	*	3·3
	A24	
5	7·1	−7·2
3	8·1	−8·8
7	7·0	−7·2
5	4·9	4·5
4	6·8	6·4
3	5·4	−6·0
2	13·0	11·9
1	4·5	4·8
0	7·2	−8·2
	A2$\bar{5}$	
1	7·5	5·9
	A25	
$\bar{11}$	5·7	−6·2
$\bar{10}$	5·8	−6·6
9	5·0	−4·5
8	4·1	−5·1
7	4·1	−4·6
6	5·7	5·5
5	8·1	5·5
4	4·2	3·6
3	7·0	7·4
1	6·5	−6·1
0	12·4	−11·1
1	7·7	−7·6
2	7·0	−7·2
	A26	
$\bar{10}$	7·0	−8·2
8	6·2	7·4
8	4·1	4·9
7	3·6	3·5
6	5·0	5·9
5	10·5	11·0
3	7·7	−8·3
1	4·3	−6·1
0	7·1	−8·5
1	8·3	−8·5
4	8·1	8·8
6	10·9	12·4
	A27	
9	10·7	12·6
3	5·8	6·1
2	4·8	5·9
0	6·6	−6·8
2	4·3	6·1
3	5·3	5·5

h	$\frac{1}{4}F_o$	$\frac{1}{4}F_c$
	A28	
$\bar{10}$	10·2	11·6
5	6·2	6·3
4	4·9	−5·8
3	10·6	−10·3
1	9·7	11·4
0	8·8	8·3
1	5·8	N.C.
	A29	
$\bar{11}$	6·8	−2·5
4	4·8	−4·9
A2$\bar{2}$ (Lower half of film)		
	A20	
2	6·6	9·0
3	11·5	15·8
4	4·5	−7·3
5	11·4	15·4
8	3·2	−2·9
9	8·4	−9·1
11	5·9	−7·3
	A2$\bar{1}$	
2	12·1	10·3
3	10·6	7·3
4	6·2	−5·6
6	3·5	2·8
7	3·2	4·0
8	4·6	−5·2
9	7·3	−7·9
10	5·4	−6·4
11	4·5	−5·1
	A21	
0	17·0	12·9
1	29·0	20·4
2	13·9	10·9
6	4·3	−4·1
7	10·8	−10·1
8	9·7	−10·3
10	11·9	12·6
11	10·9	11·2
	A2$\bar{2}$	
2	2·6	4·3
3	3·9	−3·2
5	4·9	−4·4
6	16·9	16·0
7	5·1	5·9
8	3·1	3·2
11	8·8	−8·8
13	4·7	−5·1
	A22	
1	18·1	15·2
0	11·1	8·3
1	13·4	11·6
2	22·6	19·4
3	9·4	8·7

h	$\frac{1}{4}F_o$	$\frac{1}{4}F_c$
	A22	
5	10·8	−9·1
6	6·9	−7·3
7	5·1	−5·1
8	4·3	−3·6
11	6·7	6·7
12	10·0	9·8
	A2$\bar{3}$	
2	6·5	−5·8
3	6·9	−6·9
4	8·9	−7·6
5	5·4	−4·9
7	5·5	6·1
8	4·6	4·8
9	4·8	5·2
10	10·5	11·3
	A23	
2	6·9	−7·7
3	7·3	−7·0
6	5·4	−5·9
	A2$\bar{1}$	
3	6·5	−7·2
4	7·8	−7·6
5	11·3	−9·3
6	4·7	−5·0
8	12·3	12·0
9	12·8	12·3
10	5·9	6·7
11	7·6	8·1
12	6·4	−8·3
	A24	
1	21·2	−19·3
2	6·3	−6·5
6	4·8	−6·3
7	8·0	8·6
	A2$\bar{5}$	
0	*	11·1
1	*	5·6
2	*	0·6
3	*	−0·7
4	10·7	−10·0
10	4·8	6·5
11	7·6	9·3
	A25	
6	4·8	5·2
7	6·4	7·6
	A2$\bar{6}$	
8	4·8	−5·8
9	3·5	−5·3
	A2$\bar{7}$	
8	5·9	−7·9
9	3·0	−6·1
10	3·2	−4·4

carbon atom, C(7), a plausible emendation of the y-co-ordinate was made on chemical grounds: the value resulting from the least-squares refinement would have put this atom 0·06 Å out of the plane of its benzene ring and given less probable lengths for the two C–O bonds; since the co-ordinate is near to $\frac{1}{4}$, its value is insensitive to the $h1l$-data, and hence it seemed valid to make the small modification embodied in Table 3 to bring the atom into the plane. This change has no appreciable effect on R.

The accuracy of the analysis was assessed from the least-squares residuals. The programme used involves 9 parameters for each atom, so that, including a scaling factor, altogether 226 parameters were determined. Against these were some 750 observed reflexions; but for the y-co-ordinates the $h0l$-reflexions provide no useful information, and the excess of observations over parameters is then less adequate. The standard deviations (σ) were derived by the usual formula. They will be a little inflated because unobserved reflexions were included only for the most unfavourable terms. To take account of the σ-values for all 75 individual positional

parameters was not deemed justifiable in view of the modest excess of observations; and the values shown in Table 4 are averages for atoms of each chemical type. Also shown are derived values of σ for bond-lengths. For bond-angles σ is about 2°. The more important of these dimensions are embodied in Fig. 4. Later it will be convenient to discuss this structure in terms of a " representative molecule; " it is comprised by the atoms with the co-ordinates listed in Table 3 for nitrobenzoate residue *D*, and for *E* by the atoms with co-ordinates listed for x and z but with y increased to $y+1$. When two contacts between a given pair of atoms are noted in Fig. 4, one of them refers to a second representative molecule, one primitive translation removed along y; the distance corresponding to this latter molecule is shown in parentheses. Values of $|F_o|$ and F_c are listed in Table 5.

Discussion

The first object of this work was to discover whether the structures of these acid nitrobenzoates differ in the manner suggested by their spectra. The suggestion has been verified and the structure of the *o*-nitrobenzoate has already been described. Attention can now be shifted to potassium hydrogen di-*p*-nitrobenzoate, the details of whose structure are of some interest in themselves.

The two nitrobenzoate residues are crystallographically distinct. That marked *D* in Figs. 3 and 4 is the anion, X^-; that marked *E* the neutral molecule, HX. The evidence for this assignment is as follows: *D* makes contacts with potassium ions through three of its oxygen atoms—O(5) and O(6) belonging to its carboxyl group, and O(8) of its nitro-group—whilst *E* makes contact only through one carboxylic atom, O(1); the dimensions of the two carboxyl groups differ in the sense required: *e.g.*, *D* has the C–O lengths nearly equal, *E* has them unequal; in the final difference synthesis, a peak of height 1·0 electron per Å^2 appeared nearly on the line O(2) · · · O(5) and nearly in the position appropriate to a hydrogen atom covalently linked to O(2).

Both benzenoid rings are substantially planar. For ring *E* the mean plane is given by the equation,

$$-0{\cdot}374X' + 0{\cdot}809Y' - 0{\cdot}213Z' = -2{\cdot}092$$

and for *D* by

$$-0{\cdot}187X' + 0{\cdot}795Y' - 0{\cdot}420Z' = 1{\cdot}473$$

The average deviations of the carbon atoms from these planes are 0·01 Å for *D* and 0·03 Å for *E*. In each residue the nitro- and carboxyl groups are slightly, but significantly, twisted out of the plane of the benzene ring; the twists are in the same direction about the longest axis of each residue, and they amount to 5° for both groups in *D*, and to 5° for NO_2 and 10° for CO_2^- in *E*. The two potassium ions related by the centre of inversion chosen as origin are separated by 4·71 Å, and those related by the centre at $0\frac{1}{2}0$ by 4·20 Å. These close approaches are mitigated by an environment of oxygen atoms. Each potassium is surrounded by six oxygen atoms of six different nitrobenzoate groups, the oxygen atoms lying at the corners of a distorted octahedron. That one K · · · O contact is with oxygen of a nitro-group is noteworthy.

The hydrogen bond, with O · · · O = 2·492 ± 0·020 Å, joins residues *D* and *E* together to give a well-defined anionic complex. This complex corresponds to the representative molecule. In contrast to the symmetrical anionic complex in the *o*-nitrobenzoate and in other acid salts of type *A*, which may be formulated as $\overbrace{\bar{X}\text{–}H\text{–}\bar{X}}$, this complex is unsymmetrical and may be formulated as $\bar{X}\cdots H\text{–}X$. Such units are linked together into infinite columns in the y-direction by electrovalent forces between their carboxylic oxygen atoms and the ascending zig-zag of potassium ions; and the parallel columns are tied together in the z-direction because residue *D* makes contact at either end with potassium

ions. Thus are constituted strongly bound, infinite layers parallel to (100), which is the prominent morphological plane. In keeping with the ready cleavage, only van der Waals forces operate between the layers, though the fit between neighbouring layers is a good one: the protuberant *E*-residue of one layer occupies the indentation between two *E*-residues of the next, as can be seen in Figs. 3 and 4. Intermolecular contacts less than 3·8 Å have been noted in Fig. 4. Only one calls for comment—that of 3·28 Å between O(2) and C(14). The aromatic hydrogen atom should be about 2·95 Å from the oxygen. Similarly short contact distances have been reported previously.[11]

The hydrogen bond is " very short," and indeed shorter than the average (~2·5 Å) for all the salts of type *A* so far studied. This proves that mere shortness of hydrogen bonding is not the cause of the spectral anomaly shown by the latter. Some other cause must be sought; and two facts, implicit in the previous paragraph, may now be emphasised:

(1) The hydrogen-bonded unit (−Y$\bar{H}$Y−, where Y is a carboxyl groups, or part of one) in the *p*-nitrobenzoate is unsymmetrical, whereas the unit in type *A* acid salts is effectively symmetrical; and (2) these units in the *p*-nitrobenzoate form part of a hydrogen bond–

electrovalency sequence (· · · Y$\bar{H}$Y $\overset{+}{M}$ Y$\bar{H}$Y $\overset{+}{M}$ Y$\bar{H}$Y · · ·) that runs in only *one* dimension, as spiral chains, whereas the units in type *A* acid salts belong to sequences that extend infinitely in *two* or *three* dimensions (as nets or lattices). An explanation of the spectral anomaly must take account of these special features. A discussion of them is essayed in Part VI.

In the later stages of this work most of the calculations were done on the Glasgow University DEUCE computer, and we are indebted to the Director of the Computing Laboratory for this facility. The large-scale crystallographic programmes, developed by Dr. J. S. Rollett, were made available by courtesy of the Superintendent of the Mathematics Division of the National Physical Laboratory. We are also indebted to the University of Sauger (India) for granting study-leave and financial assistance to H. N. S. We appreciate the interest shown in this work by Professor J. M. Robertson, F.R.S.

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[*Received, June 21st,* 1960.]

[11] Abrahams and Sime, *Acta Cryst.*, 1960, **13**, 1.

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230. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part VI.* Sodium Hydrogen Diacetate.*

By J. C. Speakman and H. H. Mills.

Sodium hydrogen diacetate is one of the simplest acid salts of type *A* (see Part V), and it displays the corresponding spectral anomaly in a pronounced form. It crystallises in the cubic system, with 24 $NaH(C_2H_3O_2)_2$ molecules in a unit cell, of edge 15·9$_2$ Å, belonging to the space group *Ia*3. Its crystal structure has now been determined, and refined by three-dimensional methods. The sodium ions are crystallographically of two kinds, Na(1) and Na(2), and they are present—3·3 Å apart—as linear triads, Na(2) · · · Na(1) · · · Na(2), lying along a three-fold axis. The two acetate residues in the formula are crystallographically equivalent, being related by a two-fold axis, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. This bond is of the symmetrical type, with $O \cdots O = 2{\cdot}44_4 \pm 0{\cdot}010$ Å. These hydrogen-bonded units are linked together by the interposition of sodium ions to give infinite three-dimensional sequences. Therefore any vibration of the proton in one unit might interact with the motions of protons in other units extending over a wide region of the crystal. The significance of the " very short," and quasi-symmetrical, hydrogen bond is discussed.

Acid salts of acetic acid have been known since the time of Thomas Thomson, but sodium hydrogen diacetate (" sodium binacetate "), $NaH(C_2H_3O_2)_2$, was not discovered until 1877, when it was independently described by Villiers [1] and Lescoeur.[2] The compound crystallises in the cubic system, and its morphology was examined by Haushofer.[3] In 1922 Wyckoff [4] made it the subject of the earliest explicit determination, by *X*-rays, of a complex space group. The historian may appreciate the contrast between Lescoeur's surprise that a compound of relatively complex composition (" $C^4H^3NaO^4$,$C^4H^4O^4$ ") should crystallise in the simplest system and Wyckoff's comment that " such a relatively simple (organic) substance as this sodium acid acetate has . . . a very complicated (crystal) structure."

As explained in Part V, the crystalline acid salts examined in this laboratory fall into two classes, *A* and *B*, between which differences of structural type are paralleled by differences of infrared spectra. Sodium hydrogen diacetate shows the anomalous infrared spectrum, characteristic of type *A* salts, to a pronounced degree (see Fig. 1). For this reason, as well as because it is the simplest acid salt of almost the simplest carboxylic acid, its structural analysis was of unusual interest. A preliminary account of this work has appeared.[5]

Experimental

Preparation, Infrared Spectrum, and Crystal Data.—Sodium hydrogen diacetate separates as well-formed, and evidently cubic, crystals when a solution of acetic acid and half an equivalent of sodium hydroxide in water, or aqueous alcohol, is allowed to cool or evaporate. The crystals quickly become opaque owing to a superficial loss of acetic acid; but the bulk of the crystal remains unchanged for days or weeks (depending on the atmospheric conditions), and there is no difficulty in obtaining adequate *X*-ray patterns.

The infrared spectrum of the solid material was recorded both for a Nujol mull and for a KCl disc. There is some difficulty in obtaining a spectrum that is definitive in the high-frequency region; for, if a large, freshly prepared, single crystal is used for preparing the sample,

* Part V, preceding paper.

[1] Villiers, *Compt. rend.*, 1877, **84**, 774; 1877, **85**, 755.
[2] Lescoeur, *Compt. rend.*, 1877, **84**, 1029; *Ann. Chim. Phys.*, 1893, **28**, 237.
[3] Haushofer, *Z. Krist.*, 1880, **4**, 572.
[4] Wyckoff, *Amer. J. Sci.*, 1922, **4**, 175.
[5] Speakman, *Proc. Chem. Soc.*, 1959, 316.

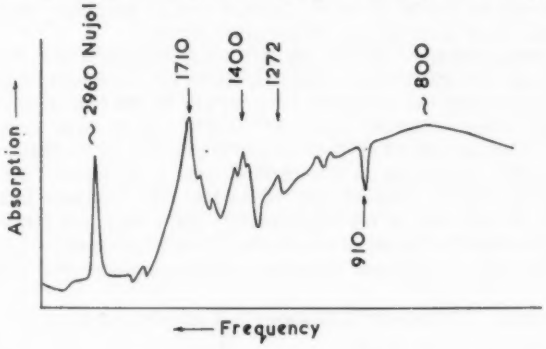
it may contain mother-liquor, absorbed or occluded; whilst, if small and properly dried crystals are used, the superficial decomposition may affect the spectrum. However the main features of the spectrum shown in Fig. 1 (Nujol mull) are reproducible. (Dr. Hadži has provided a spectrum from Ljubljana, and it is essentially identical with that recorded in Glasgow.)

The unit-cell parameter was determined by single-crystal rotation photographs, against calcite as reference substance, and by powder photographs against metallic copper. Systematic absences were determined from moving-film photographs. Copper $K\alpha$-radiation was used throughout.

$NaH(C_2H_3O_2)_2$, $M = 142{\cdot}09$, cubic diakisdodecahedral, class $m3$, $a = 15{\cdot}92 \pm 0{\cdot}01$ Å, $U = 4035$ Å^3, $D_m = 1{\cdot}40_0$ (by flotation in chlorobenzene–chloroform), $Z = 24$, $D_c = 1{\cdot}403$, $F(000) = 1776$, absorption coefficient for X-rays 17·6 cm.$^{-1}$.

Absent reflexions. These are $hk0$ when h or k is odd (and correspondingly for $h0l$ and $0kl$) and hkl when $(h + k + l)$ is odd; they uniquely indicate the space group, $Ia3$ (T_h^7, No. 206), as found by Wyckoff. The implication is that the sodium and acidic hydrogen atoms are in special positions, and the others in 48-fold, general positions.

FIG. 1. *Infrared spectrum of sodium hydrogen diacetate, solid in Nujol mull.*



Determination of the Structure.—The space group $Ia3$ is centro-symmetric, and the phase problem reduces to one of sign-determination. To find the gross structure of this crystal, it suffices to fix the positions of only five atoms, these positions being defined by only thirteen parameters. Nevertheless the problem proved difficult, for the following reasons: (1) the high symmetry causes there to be a large number of atoms in the cell, and results in an absence of reflexions of relatively high intensity; the highest unitary structure amplitude appears to be 0·41 for 7,8,13, a reflexion which had not been recorded until the later stages of the refinement, and only one or two others exceed 0·3. (2) The sodium atoms are not heavy enough to dominate the X-ray scattering; and it is impossible to replace them isomorphously. (3) Until a late stage, only two-dimensional methods of analysis were readily available. Through the courtesy of Professor Ray Pepinsky, a three-dimensional Patterson synthesis was computed on XRAC during 1958. That this synthesis did not lead to a ready elucidation of the structure must be attributed to the high symmetry, which causes superpositions of many vector-peaks in some positions, so that the recognition of individually significant peaks is difficult. [For instance, the most heavily weighted vector-peak is that between Na(1) and Na(2), and no less than 8 of these vectors coincide to yield a Patterson peak at $u = v = w \approx 0{\cdot}120$.' *A posteriori* this peak can be recognised, but it makes only an insignificant appearance in the appropriate Patterson section.] The phase problem was in fact finally solved by simple trial, though it became possible to advance from an approximately correct trial-structure only when facilities were to hand for the rapid calculation of three-dimensional electron-density syntheses. These facilities were provided on the Glasgow University DEUCE computer by way of the crystallographic programmes developed by Dr. J. S. Rollett.

Besides 48-fold, general positions—(*e*) of the *International Tables*—the space group $Ia3$ affords 24-fold positions (*d*) on two-fold axes, 16-fold positions (*c*) on three-fold axes, and 8-fold positions (*a*) and (*b*) at centres of inversion ($\bar{3}$) on the three-fold axes. The 24 acidic hydrogen

atoms can hardly be located elsewhere than on the two-fold axes—unless they be disordered in some way—which implies that they are probably involved in a crystallographically symmetrical hydrogen bond. The 24 sodium atoms (or ions) might also occupy positions (*d*), but there is the alternative possibility that they might be of two crystallographically distinct kinds—8 Na(1) in positions (*a*) or (*b*), and 16 Na(2) in positions (*c*). The former arrangement, thought to be more likely *a priori*, was assumed in many trial structures; the latter proved to be correct.

With positions (*a*) chosen for Na(1), two such ions are about 14 Å apart at the corner (0,0,0) and centre $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ of the unit cell. A three-fold axis along a body-diagonal joins them, with an unoccupied centre of symmetry between them at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$; and on this axis twice as many Na(2) ions are to be sited. Packing considerations suggested that the Na(2) ions might lie about 3 Å on either side of Na(1), thus constituting a " triad " of sodium ions, Na(2) · · · Na(1) · · · Na(2); and that the acetate group must be placed so that a triangle of oxygen atoms, generated by operation of the three-fold axis on O(1), can cushion the tightly packed cations, and so that its other oxygen atom, O(2), is close enough to a two-fold axis to enter into hydrogen bonding across that axis *via* the acidic hydrogen. On this basis it was possible to construct trial structures, one (at least) of which was sufficiently close to the truth to enable the (three-dimensional) Fourier-series method to be applied successfully. This starting structure had the sodium atoms and one oxygen atom nearly in their correct positions; refinement proceeded satisfactorily despite errors in the placings of the other atoms.

Refinements.—Intensities were derived visually from multiple-film exposures in the usual way. Altogether some 760 independent reflexions should be accessible to copper radiation. In the earlier stages, refinement was based on some, or all, of 195 reflexions recorded on photographs covering the reciprocal-lattice nets, $hk0 \cdots hk5$. In the later stages, when the nets $hk6 \cdots hk8$ and the diagonal net $h,k,(2-h-k)$ were also included, 323 reflexions were observed—43% of those accessible. If the region of reciprocal space is curtailed at $2 \sin \theta = 1{\cdot}58$, which corresponds to half the volume theoretically accessible, 65% coverage is attained. Though far from complete, the coverage is fairly satisfactory for a structure composed only of light atoms; it represents a nine-fold excess of observations over all parameters. During the scrutiny of these photographs, many equivalent reflexions were measured several times. This made it

TABLE 1. *Progress of refinement and atomic co-ordinates.*

Phase	1	2	3	4	5
Procedure	Electron-density syntheses	6 Cycles of L-S (O & C only)	3 Cycles of L-S [With Na(2)]	4 Cycles of L-S	2 Cycles of L-S
No. of terms	130	195	195	319	323 +29 unobsd.
Co-ordinates					
Na(2)	0·1196	(0·1195)	0·1196	0·1195	0·11956 *
O(1) x	0·0325	0·0326	0·0320	0·0324	0·03213
y	0·3788	0·3903	0·3904	0·3913	0·39144
z	0·0963	0·0999	0·1006	0·0999	0·09994
O(2) x	0·0769	0·0736	0·0742	0·0749	0·07525
y	0·2629	0·2651	0·2659	0·2652	0·26521
z	0·1362	0·1386	0·1389	0·1396	0·13970
C(1) x	0·091	0·0910	0·0903	0·0899	0·08964
y	0·336	0·3365	0·3371	0·3394	0·33971
z	0·115	0·1117	0·1115	0·1103	0·11036
C(2) x	0·174	0·1772	0·1778	0·1785	0·17885
y	0·363	0·3593	0·3583	0·3587	0·35908
z	0·090	0·0906	0·0897	0·0889	0·08904
O(2)···O(2′) (Å)	2·48	2·39 ± 0·03	2·42 ± 0·02	2·433 ± 0·013	2·444 ± 0·010
R (%) (all currently obsd. terms)	20·0	15·9	12·2	9·7	9·2

* The co-ordinates in this column represent the final values from the analysis. The origin chosen is at the centre of inversion occupied by Na(1).

possible to assess the accuracy of the mean structure amplitudes on the basis of internal consistency. The estimate was $\sigma(|F_o|) \approx 0{\cdot}09_4|F_o|$. Absorption corrections were not applied. This omission is not serious with the crystals used (having cross-section areas ~0·5 × 0·5 mm.²), but it will tend slightly to depress the values derived for the temperature factors.

The progress of refinement is summarised in Table 1, which should be self-explanatory with the aid of the following comments.

(1) In calculations of structure factors, F_c, standard atomic-scattering functions [6] were used for carbon and hydrogen. For Na^+, Freeman's [7] function was used; for oxygen, since these atoms were regarded as partially ionic, a scattering curve appropriate to $O^{\frac{1}{2}-}$ was derived by taking, at each value of sin θ, the means of his values for O and O^-. In the first phase, the isotropic Debye temperature factor, B, was taken as 2·6 Å^2 initially, and subsequently as 2·0. In later phases the least-squares (L-S) programme led to anisotropic temperature factors which were treated as variable parameters. In phase 1, $|F_o|$ values were placed on an absolute scale by correlation of $\sum|F_o|$ and $\sum|F_c|$. Subsequently the scaling factor was treated as a variable parameter in the L-S refinement.

(2) To ensure correct symmetry in electron-density syntheses, such terms as $F(hkl)$ had necessarily to be included in the triple Fourier series in all three forms, *hkl*, *klh*, and *lhk*. The structure factors for three such reflexions are equivalent however, and in the L-S refinement only one of them was needed.

(3) The L-S programme is not designed directly to handle atoms in special positions. In phase 2 therefore, refinement was restricted to oxygen and carbon atoms; the position of Na(1) is precisely fixed by the space group, whilst the single parameter needed to locate Na(2) had been well determined by the early electron-density calculations. In phase 3, however, Na(2) was introduced into the refinement. For an atom in the special position x, x, x, three identical normal equations will be developed for the co-ordinate shifts, Δx, Δy, and Δz; and, by using the Gauss–Seidel iteration for their solution, the L-S programme arrives at the erroneous result that $\Delta y = \Delta z = 0$, whilst Δx is three times its true value. The refinement could then be simply rectified by putting the new co-ordinates all equal to the mean of those produced by the programme: *i.e.*, $(x + \Delta x)$, x, x is rectified to $(x + \frac{1}{3}\Delta x)$, $(x + \frac{1}{3}\Delta x)$, $(x + \frac{1}{3}\Delta x)$. An analogous procedure was followed for the thermal parameters of Na(2). No direct refinement of the thermal parameter of Na(1) was attempted; but in the last phase it was adjusted to be smaller than those for Na(2) in a ratio suggested by its higher electron-density peak—23·9 electrons Å^{-3} against 21·7.

(4) The L-S weighting system was $\sqrt{w} = (|F_o|/F^*)$ when $|F_o| < F^*$, and $\sqrt{w} = (F^*/|F_o|)$ when $|F_o| > F^*$, where F^* was put equal to 57 (the mean value of the observed structure amplitudes). Half-shifts were generally applied.

(5) Hydrogen atoms were disregarded until phase 4, when an $(F_o - F_c)$ synthesis revealed peaks (see Fig. 5) at positions appropriate to methyl-hydrogen atoms. The appearance of these peaks suggested the presence of large thermal vibrations, as was expected, and these atoms

TABLE 2. *Atomic co-ordinates from Fourier syntheses.*

(Methyl-hydrogen atoms from difference synthesis; other atoms from final electron-density synthesis.)

	x	y	z		x	y	z
H(1)	0·204	0·402	0·136	Na(2)	0·1193	0·1193	0·1193
H(2)	0·181	0·388	0·027	O(1)	0·0321	0·3906	0·0994
H(3)	0·215	0·301	0·089	O(2)	0·0766	0·2630	0·1399
				C(1)	0·0895	0·3405	0·1103
				C(2)	0·1775	0·3601	0·0899

were included in subsequent F_c-calculations, though not in L-S refinement, with an isotropic B-value of 7·0 Å^2. As to the acidic hydrogen atom, a peak of height 1·9 electrons Å^{-3} appeared in the ordinary electron-density section at $z = 33/240$, and at the expected position $x = 0$, $y = \frac{1}{4}$ (see Fig. 2). This height is surprising, and it may have been enhanced by the tendency for residual errors to produce small false peaks at special positions. However, the peak is undoubtedly due principally to the hydrogen atom, and for it a lower B-value of 4·0 Å^2 was adopted. This atom was included in subsequent F_c-calculations, and its region became satisfactorily flattened in an $(F_o - F_c)$ synthesis. The co-ordinates for the methyl-hydrogen atoms, listed in Table 2, were chosen to be consistent with Fig. 5 whilst maintaining trigonal symmetry for the methyl group. No great accuracy is claimed for them.

(6) At phase 5 account was taken of the unobserved reflexions. Structure amplitudes were

[6] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[7] Freeman, *Acta Cryst.*, 1959, **12**, 261.

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calculated for all such terms out to $2 \sin \theta = 1{\cdot}58$, and in 29 cases $|F_c|$ implied that the reflexion should have been observable. These terms were then included in later L-S refinement, each with a value of $|F_o|$ equal to half the minimum locally observable. When these reflexions are

TABLE 3. *Standard deviations of the final atomic co-ordinates* (Å).

	(*x*)	(*y*)	(*z*)		(*x*)	(*y*)	(*z*)
Na(2)	0·0094	0·0094	0·0094	C(1)	0·0073	0·0082	00081
O(1)	0·0055	0·0058	0·0063	C(2)	0·0086	0·0108	0·0093
O(2)	0·0053	0·0053	0·0063				

TABLE 4. *Thermal parameters* ($b_{ij} \times 10^5$).

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Na(1)	228	228	228	—	—	—
Na(2)	268	268	268	—	—	—
O(1)	306	330	507	245	23	48
O(2)	279	248	675	−48	−184	65
C(1)	226	305	250	−157	−134	65
C(2)	273	632	571	89	445	−105

TABLE 5. *Observed structure amplitudes and calculated structure factors.*

h	*l*	$\lvert F_o \rvert$	F_c	*h*	*l*	$\lvert F_o \rvert$	F_c	*h*	*l*	$\lvert F_o \rvert$	F_c	*h*	*l*	$\lvert F_o \rvert$	F_c
		0*kl*				1*kl*				1*kl*				2*kl*	
0	2	144	+158	1	2	110	−121	19	2	25	−39		5	97	−99
	4	291	−508		4	70	−72						7	38	−47
	6	163	−167		6	168	+200			2*kl*			11	33	+59
	8	223	+253		8	76	+72	2	2	136	+148	14	4	59	+62
	10	115	+121		10	52	−51		4	94	+92		6	38	+51
	12	30	+36		12	30	−29		8	24	+21			3*kl*	
	14	59	−59		14	37	+45		10	73	+81				
	18	24	+28	2	3	82	−90		12	41	+45	3	6	107	−105
2	2	39	+28		5	15	+18		18	29	+24		8	50	+47
	4	166	+192		7	43	+43	3	3	130	−138		10	39	+37
	6	20	−7		9	38	+34		5	118	−116		14	77	−80
	8	57	+57		11	30	−29		7	64	+63	4	7	51	−51
	10	94	+90		13	39	+45		9	78	+75		9	37	+34
	12	53	+57		15	35	−37		11	33	−16	5	4	38	+32
	14	52	−45		19	30	+36		13	63	−65		6	47	+40
	18	39	+43	3	2	100	+104	4	4	24	+32		8	30	+21
4	2	96	−96		4	113	−106		6	21	+21		10	55	−49
	4	199	+206		6	117	+118		10	29	+23		16	36	+35
	6	220	+238		8	115	+113		12	69	+70	6	5	49	−47
	8	56	+50		12	44	−42		14	69	+72		7	105	+109
	10	47	−43		14	57	+57		16	29	+30		9	85	+87
	12	26	+13	4	3	26	+21	5	3	131	−126		11	68	−63
	14	70	+79		7	59	−54		5	87	−96		13	74	−78
	16	29	+33		9	28	+20		7	101	−96		4	32	+23
	18	18	+22		13	44	+47		9	81	+79		6	61	+55
6	2	162	+166	5	2	109	+116		11	30	−21		10	32	−52
	6	34	−24		4	57	+60		13	59	−59		14	59	+55
	8	28	+20		6	43	−44	6	4	91	+99	8	5	77	−71
	10	105	+97		8	114	−111		6	75	+74		7	19	−21
	14	63	+65		10	35	+39		8	71	+64		9	49	+42
	16	46	+48		12	69	+67		10	44	+42		13	70	−66
	18	21	+22		16	57	−64		12	29	+17	9	4	36	−29
8	2	173	+193	6	3	64	−68		16	32	+27	10	7	36	−34
	4	137	−133		5	108	−108		18	23	+24		9	38	−30
	6	43	−34		9	54	+58	7	3	59	−64		11	43	+42
	8	70	+66		13	19	−22		5	98	+99	11	4	55	−58
	10	101	+111		19	12	−23		7	49	−41		8	40	+28
	18	20	+22	7	2	172	+186		9	38	−36		10	45	+45
	18	13	−4		4	20	+17		11	56	−58		12	39	−38
10	2	52	+50		6	203	−202		13	33	+29	14	5	60	−55
	4	55	+53		8	65	−64		15	32	+34		7	51	+50
	6	74	+84		10	65	+66	8	4	48	+47		9	52	+41
	8	33	+32		14	40	−41		6	77	+69			4*kl*	
	10	30	+29	8	5	56	−50		8	85	+76				
	12	21	+19		7	21	+11		10	29	+28	4	4	33	+51
	14	20	−19		9	45	+46		18	27	+24		6	135	+133
12	2	39	−39		11	30	+37	9	5	71	+66		8	127	+120
	4	108	+108		13	66	−71		7	48	+48		10	30	+24
	6	109	+108		2	109	−105		11	36	−35		12	41	−29
	10	52	−49		4	49	+51		13	31	+28		14	22	−30
	12	48	+46		8	42	−50		15	47	+46		16	22	+29
	14	20	+18		10	31	−22	10	4	36	+35	5	5	48	−47
14	2	27	−17		12	31	+28		10	36	+36		9	32	−29
	4	127	+130	10	3	33	+34		12	30	+41		11	30	−27
	6	24	+16		5	34	+30	11	3	36	+36	6	6	84	+76
	8	26	−22		9	32	−37		5	33	+30		10	32	−36
	12	52	+56		11	32	+30		9	29	−22		12	64	+62
	14	33	+40	13	2	36	+45		11	65	+76	7	5	21	−26
16	2	29	+12	8	29	+29	12	6	44	+35		7	42	+39	
	8	45	+41	14	3	44	−49		8	19	+27	8	12	102	+95
18	2	30	+43		5	43	−52		14	24	+29		14	45	+41
	10	29	+36		7	19	+22								
20	2	24	+35	15	2	43	+42	13	3	100	+99				

TABLE 5. (*Continued.*)

h	*c*	$\|F_o\|$	F_c	*h*	*c*	$\|F_o\|$	F_c	*h*	*c*	$\|F_o\|$	F_c	*h*	*c*	$\|F_o\|$	F_c
		4*kl*				5*kl*				6*kl*				7*kl*	
9	5	32	−30		10	34	−31		14	49	+42		12	19	+18
	7	26	+18		12	43	−45	7	9	32	−32		14	19	−21
	9	40	+34		16	38	+46		11	36	+38		16	19	−14
10	8	72	+64	6	9	85	−79	8	8	21	+22	8	9	75	−75
	10	67	+59		13	42	+46		10	48	+61		13	82	+84
11	5	69	+67		15	32	+30		12	43	+38	9	8	26	+34
	7	37	−33	7	6	146	+140	9	7	84	−81	11	10	52	−52
	9	38	−35		8	60	+48	10	8	34	+36	12	11	19	−18
	11	33	+24		10	44	−40		10	60	+64		13	34	−43
12	8	70	+66		14	39	+43		12	32	+29	14	9	26	−30
	10	66	+63	8	7	21	+21	11	11	44	−32	15	10	29	+24
	12	32	−31		11	46	−50	12	10	38	+29				
13	5	40	−29	9	8	68	+61	13	7	52	+49			8*kl*	
	7	44	−40	10	9	49	+57		11	47	−54	8	8	56	+55
14	6	35	+28		11	40	−33	14	8	56	+57		10	52	+49
	8	31	+26	11	12	21	−27		10	21	−7		12	19	−23
	10	29	+33	12	7	45	−53	16	8	23	+27	9	9	48	−53
16	6	27	+33		9	39	+30		10	21	+22		13	38	+36
					11	34	+29					11	11	21	−32
		5*kl*				6*kl*				7*kl*		13	11	21	−25
5	6	52	+50	6	6	133	+122	7	8	54	−30	16	8	42	+43
	8	73	+67		8	28	+26		10	19	+21				

Unobserved terms used in phase 5.

h	*k*	*l*	$\|F_o\|$	F_c	*h*	*k*	*l*	$\|F_o\|$	F_c	*h*	*k*	*l*	$\|F_o\|$	F_c	*h*	*k*		$\|F_o\|$	F_c
0	8	14	<19	+17	1	11	8	<20	+22	3	4	13	<20	+24	5	9	10	<20	+19
0	16	4	<19	+19	1	11	10	<20	−16	3	4	15	<19	−31	5	9	12	<19	−32
0	18	8	<14	+37	1	12	9	<20	−29	3	7	12	<20	+18	5	13	8	<19	−29
0	20	4	<12	+29	1	15	6	<19	−16	3	9	10	<20	+20	6	9	11	<20	+33
1	4	11	<18	−20	2	5	15	<19	−30	3	13	6	<20	+17	6	12	8	<19	+18
1	6	11	<19	−15	2	13	9	<19	+25	3	15	4	<19	+38	7	10	9	<20	+18
1	11	4	<18	+17	2	16	2	<19	+19	4	9	13	<19	−16	9	9	10	<19	−34
1	11	6	<18	+16															

taken into account, the final R-value rises from 9·2 to 10·9%. Since only the more unfavourable of the unobserved terms have thus been included, the value of R is a conservative one. Either of these values approximates to the estimated standard deviation of $|F_o|$, which suggests that the analysis has been refined as far as the accuracy of the observational data warrants.

The final co-ordinates are those listed in the right-hand column of Table 1. The atoms—particularly the acetate group—corresponding to these co-ordinates are taken as the " representative molecule," which is the one whose atoms are denoted by unprimed numerals in Fig. 4. Relevant standard deviations, worked out from the L–S residuals in the usual way, are listed in Table 3. Thermal parameters are in Table 4; they are values of b_{ij} in the equation,

$$\exp(-B\sin^2\theta/\lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{31}lh)}$$

The final values of $|F_o|$ and F_c are shown in Table 5. For the intense, low-order reflexion 400, $|F_c|$ always greatly exceeded $|F_o|$; as the difference could reasonably be attributed to extinction, the latter was given a value substantially equal to the former in all L–S cycles after phase 3. This higher value was used in calculating R.

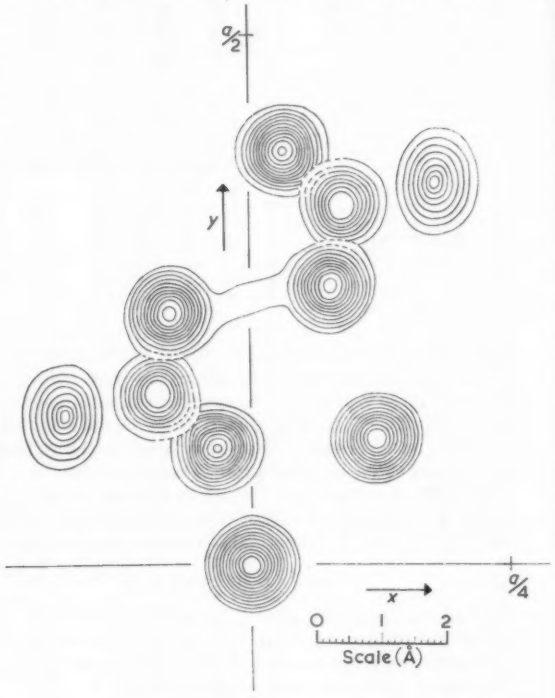
Description of the Structure

The operations of the space group produce from the representative molecule an intricate, but elegant, structure, suggested by Fig. 2 which shows part of the atomic arrangement near one corner of the unit cell. The Figure is a rough perspective of the structure, viewed nearly in the line of the cube-diagonal. Along this diagonal, which embodies a three-fold axis, is a triad of sodium ions, Na(2) · · · Na(1) · · · Na(2), with Na(1) at the corner of the cube, which is a centre of inversion and has been chosen as origin. Parallel to the cube-edges, and a quarter of the way along each face, are three two-fold axes, as shown. Two equivalent acetate groups lie on either side of each such axis; joined by the hydrogen bond (shown as a broken line) involving the acidic hydrogen atom, they constitute a complex anion of the form XHX^-, which has axial symmetry (2). Three such complexes are grouped round each end of the sodium triad, only the nearer three being shown in Fig. 2. Altogether twelve acetate groups make ionic contact with a given sodium triad. Of each acetate group, one oxygen atom, O(1), makes contact with a

sodium ion of either type; the other, O(2), makes contact with Na(2) of a different triad and also takes part in a hydrogen bond. In accordance with the symmetry of its point-position, Na(1) has as nearest neighbours six equidistant O(1)-atoms, arranged at the corners of a regular trigonal antiprism. (Only the nearer half of this environment appears in Fig. 2.) Na(2) also makes contact with six oxygen atoms—three O(1), three O(2); these atoms are at the corners of a less regular antiprism, though one still necessarily of

FIG. 2. *Partial view of the structure near to one corner of the unit cell. (The largest circles correspond to sodium atoms, the smallest to carbons. The "representative" acetate group is that drawn with heavy lines and with oxygen atoms bearing unprimed numerals. Hydrogen bonds are marked by broken lines. A three-fold axis and three two-fold axes are shown.)*

FIG. 3. *Electron-density sections near the centres of the sodium, oxygen, and carbon atoms. (For an interpretation see Fig. 4. The first contour-line is at 1 electron per cubic Å, with subsequent lines at unit intervals, but only alternate lines are shown for sodium.)*



trigonal symmetry. The three types of Na · · · O distances are listed in Table 6, which also gives the dimensions of the acetate group.

TABLE 6. *Interatomic distances (Å) and bond-angles, with their estimated standard deviations.*

Na(1) · · · Na(2)	3·297 ± 0·016	O(2) · · · O(2′)	2·444 ± 0·010	O(1)–C(1)–O(2)	121·65 ± 0·71°
Na(1) · · · O(1)	2·404 ± 0·011	C(1)–O(1)	1·243 ± 0·010	O(1)–C(1)–C(2)	122·27 ± 0·70°
Na(2) · · · O(1)	2·441 ± 0·011	C(1)–O(2)	1·295 ± 0·010	O(2)–C(1)–C(2)	116·08 ± 0·70°
Na(2) · · · O(2)	2·445 ± 0·011	C(1)–C(2)	1·492 ± 0·012	C(1)–O(2) · · · O(2′)	110·79 ± 0·48°

The only non-bonded contacts requiring special mention are those between methyl groups, which cluster in the general region of the centre of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, and at a distance of about 3·3 Å from it. Two pairs of methyl groups have C · · · C separations much less than the conventional van der Waals contact of 4·0 Å; identified by dotted lines in Fig. 4, the distances are 3·629 and 3·834 Å. The positions of the methyl-hydrogen

FIG. 4. *Projection of part of the structure, showing the "representative molecule" (drawn with heavier lines, atoms at* x, y, *and* z *with unprimed numerals), and the following symmetry-related acetate groups: I* $(\bar{x}, \frac{1}{2} - y, z)$; *II* (z, x, y); *III* (y, z, x); *IV* $(\frac{1}{2} - y, z, \bar{x})$; *V* $(\frac{1}{2} - z, \frac{1}{2} - x, \frac{1}{2} - y)$; *VI* $(\frac{1}{2} - x, y, \bar{z})$; *VII* $(z, \bar{x}, \frac{1}{2} - y)$.

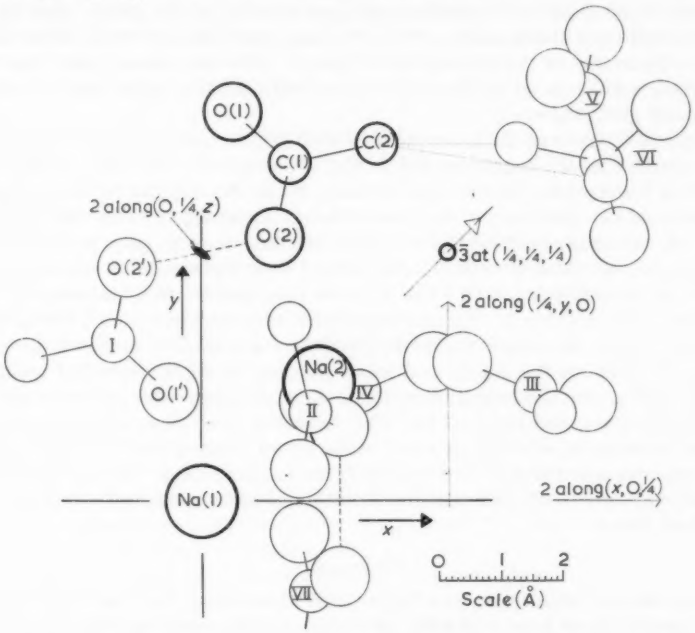
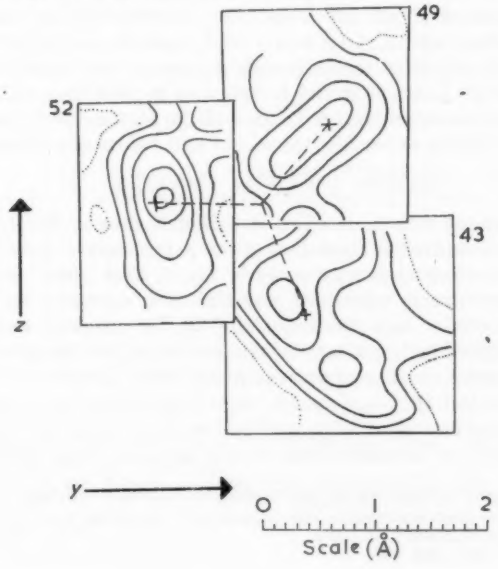


FIG. 5. *Electron-density difference map compiled from sections at* x = 49/240, 43/240, *and* 52/240, *covering the region of the methyl-hydrogen atoms.* (C–H *bonds are indicated by broken lines. Contour-line interval:* 0·1 *electron per cubic* Å, *with the zero line dotted.*)



atoms show that their conformation about the C–C axis is such as to pack a hydrogen atom of one group into the space between two hydrogens of the other. Some such interdigitation is probably necessary whenever methyl groups make unusually close contact. Where a separation of 4·0 Å has to be maintained, free rotation of the groups may be effective. The methyl-hydrogen atoms make a relatively large contribution to the 112-reflexion, and hence must lie nearly in the corresponding planes; this may have some connexion with the fact that, besides faces of the cubic form {100}, crystals sometimes occur with the tristetrahedral {112} faces.

The signs of F_c given in Table 5 were used with $|F_o|$ to compute a final electron-density synthesis, part of which is represented in Fig. 3 by sections near the centres of certain atoms. This Figure takes in the representative molecule, together with a second acetate group generated by operation of the two-fold axis along $0,\frac{1}{4},z$. The two acetate groups comprise an entire anionic complex. This electron-density map is interpreted and extended in Fig. 4. Atomic co-ordinates derived from the synthesis will be less accurate than those in the last column of Table 1, since they involve termination-of-series errors, but they are listed in Table 2. Fig. 5, composed of three sections from a three-dimensional " difference " synthesis, reveals the methyl-hydrogen atoms of the representative molecule, seen in the direction of the x-axis, and hence in a line of sight somewhat inclined to the C–C bond. Since only the sodium ions and one oxygen atom were correctly placed in the initial trial structure, and since all the other atoms of the acetate group were located by Fourier-series methods, without chemical assumptions beyond the molecular formula, the structure analysis was absolute so far as this group is concerned. It may perhaps be seen as a formal, physical confirmation of the structure of acetic acid, first explicitly drawn by Loschmidt in 1861.[8]

Discussion

This analysis has been taken to a higher level of accuracy than had been possible with any of the acid salts of type *A* studied hitherto. Certain structural features, which may be common to all these compounds, are now more firmly defined.

There are well-marked differences between the dimensions of ionised and un-ionised carboxyl groups:[9] in the former, the two C–O bond-lengths and the two C–C–O angles are substantially equal at about 1·25 Å and 118° respectively; in the latter they differ, the lengths being about 1·30 (C–OH) and 1·20 Å, and the angles about 110° (C–C–OH) and 125°. In type *A* acid salts, the carboxylic groups are equivalent and they must be of an intermediate character, which should be reflected in their dimensions. Table 6 shows that this is so. The carbon and oxygen atoms of the acetate group are coplanar: C(1) is only 0·005 Å from the plane defined by the co-ordinates of its other three atoms, *viz.*:

$$0{\cdot}62418x + 1{\cdot}47818y + 4{\cdot}01570z = 1$$

A specific study of the thermal motions in sodium hydrogen diacetate has not yet been attempted,* though a superficial inspection of the parameters in Table 4, as well as of the elongations of certain electron-density peaks in Fig. 3, shows that some of the atoms are undergoing highly anisotropic vibrations, and that their directions of greatest amplitude are those to be expected. Any movement of O(2), for instance, along x will affect the length of the hydrogen bond, and any movement along y will affect the electrovalent bonding to Na(2); hence freedom of movement should be greatest in the z-direction, and this accords with the fact that b_{33} is much larger than either b_{11} or b_{22}. Again, C(2) has higher thermal parameters than C(1), and its greatest amplitude of vibration is in a direction corresponding to libration of the anionic complex about its centre of mass.

* It is hoped that such a study will be undertaken in due course at Leeds.

[8] Loschmidt, " Konstitutions-Formeln der organischen Chemie in graphischer Darstellung," 1861 (Reprinted in Ostwald's Klassiker, No. 190).

[9] Hahn, *Z. Krist.*, 1957, **109**, 438.

The C(1)–C(2) distance in Table 6 should be increased to offset the apparent shortening effects of this torsional oscillation.[10] The magnitude of the correction has not been calculated, but it may be roughly assessed at about 0·01 Å, so as to increase the bond-length to 1·50 Å. This value differs, though not significantly, from the 1·54 ± 0·04 Å found in a careful study of solid acetic acid;[11] it is in good agreement with values found for the corresponding bonds in a series of acetyl compounds by micro-wave spectroscopy.[12]

The apparent symmetry of the hydrogen bond occurring in acid salts of type *A* was briefly discussed in Parts I, III, and V.[13] A fuller consideration may now be attempted. When a hydrogen bond is long (O · · · O > 2·7 Å), the proton is much nearer to one oxygen atom than to the other: O–H is less than H · · · O, and indeed it approximates to the normal covalent distance of about 1·0 Å. As, in a series of bonds, O · · · O diminishes overall, O–H will tend to increase and H · · · O to decrease, until, if the shortening is sufficient, they become equal.[14] What the critical O · · · O distance might be, and whether it is attained in any actual bond, is still uncertain. Coulson [15] has tentatively suggested that the upper limit for true symmetry might be about 2·45 Å. A promising field in which to search for examples is surely amongst these acid salts.

A truly symmetrical hydrogen bond would have very different properties from the normal bond, which owes its bonding energy mainly to simple coulombic forces. A major contribution would need to be added on account of delocalisation (or resonance) energy, since the canonical forms, O:H–O and O–H:O would now be equivalent, or as nearly so as the environment of the oxygen atoms allows. In most hydrogen bonds the environment is not itself symmetrical; but in type *A* acid salts (and in a few other cases such as potassium hydrogen maleate [16]—the acid salt of a ***dibasic*** acid) the setting is wholly symmetrical by crystallographic requirement. This circumstance might favour the establishment of symmetry within the bond itself.

In nearly all type *A* acid salts the absent *X*-ray reflexions do not indicate a space group unambiguously: for example, the space group of potassium hydrogen bisphenylacetate is either *I*2/*a* or the non-centrosymmetrical *Ia*. The former was chosen on indirect evidence, and the choice was assumed to have been vindicated by the success of the analysis. But there is the possible objection that the latter is the true space group, with the atomic positions of the heavier atoms merely approximating closely to the requirements of *I*2/*a*, and that of the hydrogen atom perhaps not at all, so that the crystallographic evidence for symmetry in the hydrogen bond would fail. In this context formal significance attaches to cases in which the space group is uniquely determined by the absences: sodium hydrogen diacetate is such a case, as also is potassium hydrogen di-*p*-anisate.[17]

The crystallographic symmetry element affecting the hydrogen bond in all the acid salts of type *A* studied hitherto is a centre of inversion which, taken at its face value, requires the proton to be exactly at the mid-point between the oxygen atoms. In the diacetate the element is a diad axis, wherefore the symmetry requirement could be met without the proton's being necessarily at the mid-point. It must lie on the axis, but it might be at a different *z*-level from that of the atoms O(2) and O(2′) in Fig. 4. The evidence on this point is not definitive: a three-dimensional line-synthesis along the two-fold axis shows an appropriate electron-density maximum at $z = 0{\cdot}140$, which does not differ appreciably from the co-ordinate of O(2). But this is not a sensitive method for locating a hydrogen atom linked to electronegative neighbours. The angle C(1)–O(2) · · · O(2′) is very close to tetrahedral; this angular relationship, favourable for

[10] Cruickshank, *Acta Cryst.*, 1956, **9**, 757.
[11] Jones and Templeton, *Acta Cryst.*, 1958, **11**, 484.
[12] Krisher and Wilson, *J. Chem. Phys.*, 1959, **31**, 882; see also Tabor, *ibid.*, 1957, **27**, 974.
[13] *J.*, 1949, 3357; 1954, 180; preceding paper.
[14] Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.
[15] Coulson, *Research*, 1957, **10**, 149; see also Hadži, "Hydrogen Bonding," Pergamon Press, London, 1959, p. 339.
[16] Darlow; see Hadži, ref. 15, p. 37.
[17] Skinner, Thesis, Glasgow, 1950.

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the formation of a strong hydrogen bond,[18] would not be utilised if the proton were far displaced from the O(2) · · · O(2′) line.

Neutron diffraction provides a more powerful method for locating hydrogen atoms, and reference should be made to the work of Peterson and Levy [19] on potassium hydrogen maleate and particularly to that of Bacon and Curry [20] on potassium hydrogen bisphenylacetate. In the latter the mean position is at the centre of the hydrogen bond; and, in the *b*-axial projection studied, the peak does not show signs of elongation in the O · · · O direction, as it would if the proton were executing anisotropic vibration along the bond, or if it were randomly disordered between two potential wells an appreciable distance on either side of the mid-point. (However, the proton, in a short and symmetrical hydrogen bond, might well have its greatest amplitude of vibration in a lateral direction. The vibrational ellipsoid would then be flattened along the bond-axis.) The work on the bisphenylacetate has been repeated at liquid-nitrogen temperature; [21] generally all the protonic peaks are sharpened, but that for the acidic proton still shows circular contours. The neutron-diffraction analysis, whilst not excluding the possibility of a subtly disordered situation, is most simply explained in terms of a genuinely central proton.

During refinement the O · · · O distance over the hydrogen bond in the diacetate has increased from the very low value suggested in the preliminary note (see Table 1). However, the probable limits of error have contracted, and the final results make it unlikely that the bond is longer than 2·46 Å. Certainly it is in the small group of " very short " hydrogen bonds that have been accurately measured. It appears to be longer than the bond, briefly reported to have O · · · O = 2·40 Å, in acetamide hemihydrochloride; [22] and it is longer than the bond in the hydrogen maleate anion (2·42—2·43 Å).[16] This latter is symmetrical by virtue of a crystallographic mirror-plane, so that again the proton does not necessarily lie exactly on the line between the two oxygen atoms. That this *intramolecular* hydrogen bond closes a quasi-conjugated ring of six carbon or oxygen atoms may result in its experiencing a compressional stress; were the six atoms coplanar, the natural distance separating the oxygens would be only about 1·5 Å.

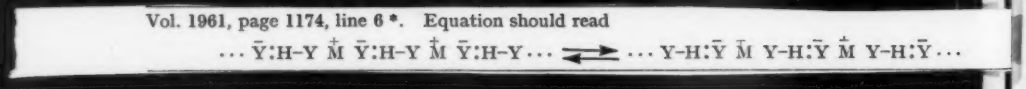
Those features of the infrared spectrum associated with the hydroxyl group, as it occurs in the normal hydrogen bond, would be greatly changed if the bond were to become symmetrical. Any vibration of the proton along the O · · · O direction would cause a large oscillation of electrostatic charge in the environment ($\bar{O}$:H–O $\rightleftharpoons$ O–H:$\bar{O}$), and this would intensify the absorption; whilst the stretching frequency—which diminishes with strength of bonding [14]—would be very low. When a number of such hydrogen-bonded units are linked together, the charge-swing in any one will affect those in neighbouring units, and they will probably enhance one another.[22] An example would be pairs of carboxylate groups (Y) joined by hydrogen bonds to give $\bar{Y}$:H–Y units, and these linked into infinite sequences *via* metallic ions:

$$\cdots \bar{Y}{:}H{-}Y\ \overset{+}{M}\ \bar{Y}{:}H{-}\overset{+}{Y}\ \bar{M}\ Y{:}H{-}Y \cdots \rightleftharpoons \cdots \bar{Y}{-}\overset{+}{H}{:}Y\ M\ \bar{Y}{-}\overset{+}{H}{:}Y\ M\ \bar{Y}{-}H{:}Y \cdots$$

This is the kind of system which obtains in the type *A* acid salts. (In the hydrogen maleate ion, by contrast, the system is intramolecularly short-circuited; and the infrared spectrum is less remarkable than those typical of class *A* salts.[23]) In most cases the $\overset{\frac{1}{2}-}{Y}$–H–$\overset{\frac{1}{2}-}{Y}$ units are linked so as to produce an infinite two-dimensional net; the bisphenylacetate, for example, has sheets of acidic hydrogen atoms and potassium ions sandwiched

[18] Donohue, *J. Phys. Chem.*, 1952, **56**, 502.
[19] Peterson and Levy, *J. Chem. Phys.*, 1958, **29**, 948.
[20] Bacon and Curry, *Acta Cryst.*, 1957, **10**, 524.
[21] Bacon and Curry, *Acta Cryst.*, 1960, **13**, 717.
[22] Albert and Badger, *J. Chem. Phys.*, 1958, **29**, 1193.
[23] Cardwell, Dunitz, and Orgel, *J.*, 1953, 3740.

Vol. 1961, page 1174, line 6 *. Equation should read



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between layers of carboxyl groups. In sodium hydrogen diacetate the cubic symmetry promotes the array of interlinked units to a three-dimensional lattice. Moreover, the chemical simplicity of the acid causes the crystal to contain a high density of such units: there are about 6 hydrogen bonds per $m\mu^3$, compared with 2·6 in the bisphenylacetate. These facts must surely constitute a basis for an explanation of the remarkable spectrum shown in Fig. 1.

We thank Professor J. M. Robertson, F.R.S., for his sustained encouragement during the elucidation of this structure; the Superintendent of the Mathematics Division of the National Physical Laboratory for permission to use the Rollett programmes; and the Department of Scientific and Industrial Research for a grant that enabled H. H. M. to take part in the later stages of this analysis.

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[*Received, June 21st,* 1960.]

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231. *Organometallic Compounds of Group II. Part III.*[1] *Unsolvated Organomagnesium Halides.*

By D. BRYCE-SMITH and G. F. COX.

Organomagnesium halides have been prepared in hydrocarbon media by reactions between various alkyl and aryl halides and magnesium in the absence of the usual ethereal catalysts. The procedure has a narrower range of application than that used conventionally, but has given yields of up to 95% in certain cases. Frequently, but not invariably, the freshly prepared hydrocarbon-soluble products have an empirical formula close to R_3Mg_2Hal, and an apparently similar material has been obtained by desolvation of an ethereal Grignard reagent. Viscosity studies have suggested that these compounds are linearly associated, with a degree of association dependent on concentration. Changes of composition with time have also been observed. Unlike ethereal Grignard reagents, the present compounds react with titanium halides to provide catalysts effective for the polymerisation of ethylene and propene at 20° and atmospheric pressure.

IN Parts I[2] and II,[1] respectively, reactions between alkyl halides and magnesium to produce free alkyl radicals and Friedel–Crafts-type alkylation of aromatic solvents were described. The present paper is concerned with conditions for the production of unsolvated organomagnesium halides by such reactions, and with some of their properties.

The excellence of Grignard's classical procedure seems largely to have discouraged attempts to prepare organomagnesium halides in the total absence of ethers and other donor catalysts (cf. Kharasch and Reinmuth[3]). Several workers have used hydrocarbon media which contained catalytic quantities of ether, dimethylaniline, etc.[3] Tschelinzeff[4] reported the preparation of Grignard reagents from some alkyl iodides in boiling xylene without added catalyst, but gave no yields or other details. Schlenk[5] obtained some high yields in benzene, but the reactions required two months for completion. König[6] obtained

[1] Part II, Bryce-Smith and Owen, *J.*, 1960, 3319.
[2] Bryce-Smith and Cox, *J.*, 1958, 1050.
[3] Kharasch and Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954, p. 50.
[4] Tschelinzeff, *Ber.*, 1904, **37**, 4534.
[5] Schlenk, *Ber.*, 1931, **64**, 739.
[6] König, *Monatsh.*, 1955, **96**, 419.

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a 42% yield of ethylmagnesium iodide in boiling benzene after three hours, and used aluminium chloride to catalyse some related preparations. Several workers [7,8] have prepared phenylmagnesium chloride by heating magnesium with an excess of chlorobenzene under pressure at *ca.* 160°, and Weissenborn [9] reports that freshly cut magnesium can be used at lower temperatures (cf. Shaw [10]), but Shoruigin *et al.*[11] found this technique to fail with various alkyl chlorides. No halogen analyses have been reported for the organomagnesium products of any of these reactions, and the formula RMgHal has been widely assumed. Little has been written of the general properties or constitution of unsolvated organomagnesium halides beyond statements that they are involatile and infusible solids, quite insoluble in hydrocarbons (but see below).[12]

An 85·5% yield of n-butylmagnesium iodide was reported in Part I [2] for a reaction between n-butyl iodide and magnesium powder in isopropylbenzene at 130°; but n-butyl chloride gave only 25% of n-butylmagnesium chloride under similar conditions. By substitution of tetrahydronaphthalene for isopropylbenzene, 85% yields of n-butylmagnesium chloride have now been readily obtained. A similar high yield of n-butylmagnesium bromide has been obtained in isopropylbenzene. These yields approximate to those reported for ethereal preparations.[13] Preliminary experiments with lower alkyl halides have given poor yields, but no attempt has been made to discover optimum conditions in these cases. No significant yields of organomagnesium products have been obtained by the use of various secondary and tertiary alkyl or benzyl halides, because of either failure to react with the metal or an excessive tendency for Wurtz-type reactions. On the other hand, phenyl halides have given good yields in deca- or tetrahydronaphthalene, or even the " paraffin oil " sold as a domestic fuel. There was no tendency for phenylation of aromatic media (cf. Part II [1]).

In general, high yields in hydrocarbon media appear to require much greater attention to the experimental conditions than is required in conventional Grignard preparations. The optimum temperature seems to be a compromise between the need to ensure a sufficiently rapid reaction of the organic halide with magnesium, and the avoidance of Wurtz-type reactions, pyrolysis of the product, and magnesium halide-catalysed alkylation of aromatic solvents.[1] This temperature appears to vary from halide to halide, and tends to be somewhat higher with chlorides than with iodides. Wurtz-type reactions are minimised by slow addition of the halide, and the use of untarnished magnesium powder rather than turnings. n-Butylmagnesium iodide was reasonably stable at 130°, whereas the chloride had completely decomposed within three days at this temperature. It is not known whether this order of stability is general. With n-butyl chloride and bromide, the tendency to alkylate aromatic media was largely avoided by the use of a sufficiently high temperature (130° rather than *ca.* 100°).[1] Reduction in the proportion of magnesium was found to promote alkylation. Thus, although butylisopropylbenzenes were formed as minor side products in the preparation of n-butylmagnesium chloride from n-butyl chloride and a slight excess of magnesium in isopropylbenzene, and no hydrogen chloride was evolved,[1] the use of a catalytic quantity of magnesium gave butylisopropylbenzenes in 52% yield, and the evolution of 75·5% of the chlorine from the halide as free hydrogen chloride.

The solubilities of organomagnesium halides in hydrocarbons varied from case to case but, contrary to previous statements,[12] were normally appreciable and sometimes quite high. From limited data, they appeared to increase in the order Cl < Br < I, and with

[7] Gilman and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 3330.
[8] Shoruigin, Issagulianz, Gussewa, Ossipowa, and Poliakowa, *Ber.*, 1931, **64**, 2584.
[9] Weissenborn, G.P. 697,420/1940.
[10] Shaw, *J. Appl. Mechanics*, 1948, **15**, 37.
[11] Schoruigin, Issagulianz, and Gussewa, *Ber.*, 1933, **66**, 1426.
[12] Rochow, Hurd, and Lewis, " The Chemistry of Organometallic Compounds," Wiley, New York, 1957, p. 88.
[13] Houben, Boedler, and Fischer, *Ber.*, 1936, **69**, 1766.

the length of the alkyl chain (methylmagnesium iodide was almost completely insoluble in isopropylbenzene), and tended to be greater in aromatic than in aliphatic hydrocarbons.

No general chemical comparison with ethereal Grignard reagents has yet been made, although the normal reactions have been observed with carbon dioxide, chlorotriphenylsilane,[2] ethyl benzoate,[14] and Michler's ketone. Preliminary work (with Mr. E. T. Blues) has indicated that unsolvated organomagnesium compounds are more active than ethereal Grignard reagents as polymerisation catalysts for common vinyl monomers and have advantages in the synthesis of organo-aluminium, -boron, and -tin compounds. Unlike ethereal Grignard reagents, the unsolvated materials have been found to react with titanium(III) or (IV) chloride to give complexes which rapidly convert ethylene or propene at 20° and atmospheric pressure into essentially linear, solid polymers of high molecular weight: the polymerisation of propene was substantially stereospecific (cf. Erusalimski *et al.*,[15] and Ziegler [16]). The use of the insoluble organomagnesium reagents described previously,[16] in conjunction with insoluble titanium(III) halides, would presumably be impracticable.

Formulæ of Organomagnesium Halides.—These have been found from the ratios of hydroxide to halide ions produced by hydrolysis of aliquot parts of the hydrocarbon solutions (base/halide ratios). In many cases, and particularly with freshly prepared solutions, the ratio has been close to 3, indicative of the empirical formula R_3Mg_2Hal (or $R_2Mg,RMgHal$). Addition of isopropylbenzene to a conventionally prepared solution of n-butylmagnesium iodide in ether, followed by removal of the ether, gave a solution of n-butylmagnesium iodide in isopropylbenzene having a base/halide ratio of 3·0, and almost identical in this respect with a solution prepared directly in isopropylbenzene from n-butyl iodide and magnesium. The use of a catalytic quantity of ether in such a preparation gave a solution having a base/halide ratio of 3·3. Less frequently, and rather irreproducibly, especially with chlorides, solutions prepared by the direct method had base/halide ratios as low as 2 or as high as 6. The irreproducibility is probably connected with changes that have been found to occur in the reagents with time. Thus, a freshly prepared solution of n-butylmagnesium chloride in isopropylbenzene had an initial base/halide ratio of 2·0: after 19 and 50 hours at 25°, the ratios were 5·0 and 14·6 respectively. These changes in composition were accompanied by a slow precipitation of solid from solution, and the corresponding solution normalities with respect to C–Mg bonds were 0·235, 0·075, and 0·085.

These observations seem not to be explained adequately by the assumption implied in Part I [2] that the solutions contain mixtures of R_2Mg and RMgHal. The presence of R_2Mg is inconsistent with the solubility data. Thus, Strohmeier [17] reported the solubilities of diphenylmagnesium and diethylmagnesium in benzene at 25° to be 0·006 and 0·016 mole per l. respectively. We found that a saturated solution of di-n-butylmagnesium in boiling isopropylbenzene at 151° contained the equivalent of 0·008 mole of Bu^n_2Mg per l., and the solubilities of anhydrous magnesium halides were too low to be measured. The present, freshly prepared n-butyl- and phenyl-magnesium halides had a much higher order of solubility, and the solutions can therefore have contained little if any free R_2Mg or $MgHal_2$. A slight uncertainty arises from a possible variation of solubility of R_2Mg with the degree of association; but this variation seems likely to be small in comparison with the observed differences, and would not readily account for the marked dependence of the solubility of freshly prepared n-butylmagnesium halides on the nature of the halogen. Further, Ph_3Mg_2Cl crystallised from tetrahydronaphthalene unchanged in its empirical composition. This behaviour would not be expected from a mixture of complexes

[14] Bryce-Smith and Skinner, unpublished work.
[15] Erusalimski, Fo-Sun, and Kabonenko, paper presented at the Symposium on Macromolecular Chemistry, Moscow, 1960.
[16] Ziegler, B.P. 801,031/1958.
[17] Strohmeier, *Ber.*, 1955, **88**, 1218.

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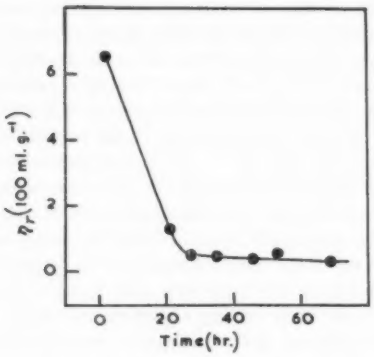
differing in their halogen content, but rather suggests either the presence of a single solute species or, more probably, a range of associated species $(Ph_3Mg_2Cl)_n$.

We suggest that the changes that can occur in these reagents with time result from a tendency for slow elimination of insoluble magnesium halide to give species which contain progressively less halogen and become correspondingly less soluble until the almost insoluble R_2Mg compound is attained. An example of this extreme production of di-n-butylmagnesium, when n-butyl bromide was heated under prolonged reflux with magnesium in benzene, was given in Part II.[1] It is noteworthy that Gilman and Brown [18] obtained dimethylmagnesium by heating methylmagnesium chloride at 190°.

Viscosity Studies.—The present solutions in hydrocarbons were normally markedly more viscous than are ethereal Grignard reagents, these being often about two-fold associated, depending on the concentration.[19] The association of $Bu^n_3Mg_2I$ has been investigated by measurements of the reduced viscosity, η_r, of a solution in isopropylbenzene. For molecular weights, M_1, up to *ca.* 8000, the intrinsic viscosity $[\eta] = k_1 + k_2M_1$. At higher molecular weights, M_2, the relation $[\eta] = k_3M_2^{\alpha}$ is generally considered



Variation, with time, of the reduced viscosity at 25° of 0·26N-n-butylmagnesium iodide in isopropylbenzene after dilution from 0·52N.

to hold. k_1, k_2, k_3, and α are constants which depend only on the solvent and the chemical and physical nature of the solute. The reduced viscosity is related to the intrinsic viscosity by the empirical equation $\eta_r = [\eta] + k_1[\eta]^2c + k_2[\eta]^3c^2 + \ldots$, where c is the concentration of the solute, and k_1, k_2, etc., are constants independent of the molecular weight of the solute. Thus, although the reduced viscosity is normally a function of the molecular weight of the solute, only relative rather than absolute values of molecular weights have been obtained owing to the difficulty of assigning values for the constants which would be applicable to a system of the present unusual type, and the unavailability of structurally analogous reference solutes of known molecular weight.

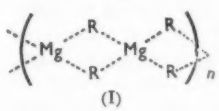
The variation in reduced viscosity with time of a 0·26N-solution of $Bu^n_3Mg_2I$ in isopropylbenzene is shown in the Figure. This solution was prepared by dilution of a 70-hours-old 0·52N-solution at zero time on the graph. It may be seen that the reduced viscosity decreased markedly over a period of about 25 hours and thereafter became almost constant. There were only slight variations in the base/halide ratio during the experiment, and no solid matter separated in the viscometer. The simplest explanation for this is that slow dissociation of an associated solute occurred after dilution, until the mean molecular weight became characteristic of the lower concentration. Changes in density with time were also observed (Table 2), but their structural implications are uncertain (particular care was taken to exclude all oxygen during this experiment in view of Slough and Ubbelohde's report of its effect in promoting the association of ethereal

[18] Gilman and Brown, *Rec. Trav. chim.*, 1929, **48**, 1133.
[19] Slough and Ubbelohde, *J.*, 1955, 108.

Grignard reagents [19]). Experiments with more concentrated solutions of n-butylmagnesium iodide were unsatisfactory owing to a tendency for separation of solid solute; this may have been a supersaturation phenomenon, or may perhaps have involved the production of less soluble material by association. The variation of molecular weight with concentration, inferred from the Figure, and found also with ethereal Grignard reagents,[19] has a parallel in Coates, Glockling, and Huck's observation [20] that the degree of association of dimethylberyllium vapour is pressure-dependent.

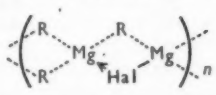
It thus appears from the available data that hydrocarbon solutions of organomagnesium halides are liable to suffer spontaneous change both through disproportionation and through changes in the degree of association, and that the relative importance of these two processes varies with the nature of the groups involved.

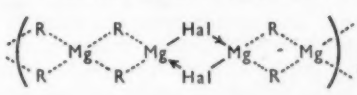
Structure.—Dimethylberyllium is known to have a linear polymeric structure,[21,20] and an analogous structure (I) has often been inferred for dialkylmagnesium compounds (electron-deficient bonds are denoted by dotted lines). For unsolvated organomagnesium halides, the present results are consistent with a range of similar structures in which there is partial replacement of R by halogen atoms. Stoicheiometry suggests that the *initial* product of reaction between magnesium and alkyl halides should be RMgHal; and in the absence of donor solvents fairly rapid association of this hypothetical intermediate is to be expected.* Since products where R/Hal $\simeq$ 1 have not yet been obtained, we assume that $MgHal_2$ is readily lost under the experimental conditions. It seems that structures having R/Hal $\simeq$ 3 provide a somewhat preferred arrangement, although the reasons for this, and for the evident instability of the initial product, remain obscure. The final product, only attained on a single occasion, appears to be a mixture of MgR_2 and $MgHal_2$. Formulæ (II) and (III) represent the repeating units in two possible structural alternatives when R/Hal = 3.



(I)

No clear decision between (II) and (III) is yet possible. No examples of " mixed " bridges of the type shown in (II) have been established although their existence has been occasionally suggested.[24] Moreover, it seems likely that the orbital overlap involved in such bridges would be a compromise resulting from differing geometric needs of R and Hal, and less than in symmetrical bridges. In the case of dimeric methylaluminium halides, $MeAlHal_2$ and Me_2AlHal, where " mixed " bridges might in principle be possible, van der

(II) 



(III)

Kelen and Herman [25] have obtained evidence from Raman spectra that bridging occurs only *via* the methyl groups. Further, the suggested disproportionation by elimination of magnesium halide can be more readily envisaged on the basis of (III) than of (II). Formula (III) is therefore slightly preferred.

Experimental

Oxygen-free nitrogen (B.O.C. " White Spot ") was used in all preparations, and for the viscosity experiments was further purified over heated copper. Hydrocarbon solvents were

* In view of the long-established usage of " RMgHal " as a shorthand term for Grignard reagents, it is noteworthy that no unsolvated compound of this empirical formula has yet been shown to exist. The closest approach is found in BrMg·C≡C·MgBr which, remarkably, is reported not to form an ether complex under the usual conditions.[22] Alkylmercuric halides appear to provide the only monomeric examples of this structural type in Group II.[23]

[20] Coates, Glockling, and Huck, *J.*, 1952, 4496.
[21] Snow and Rundle, *Acta Cryst.*, 1957, **4**, 348.
[22] Kleinfeller, *Ber.*, 1929, **62**, 2736.
[23] Dessy and Lee, *J. Amer. Chem. Soc.*, 1960, **82**, 689.
[24] Ref. 12, p. 92.
[25] van der Kelen and Herman, *Bull. Soc. chim. belges*, 1956, **65**, 362.

dry (CaH_2) and peroxide-free, and were redistilled immediately before use. Magnesium was used in the form of bright powder (*ca.* 150 mesh) and this was found much superior to the usual turnings. Turnings were used where indicated when suitable powder was temporarily unavailable, but not from choice. Mixtures were vigorously stirred. Initiation by a trace of

TABLE 1. *Preparation and analyses of n-butyl- and phenyl-magnesium halides in hydrocarbons.*

Experiment no.	1	2					3	4
Organic halide	n-BuI	n-BuI					n-BuI	n-BuBr
Amount of halide (mole)	0·071	0·080					0·070	0·080
Solvent	C [a]	C [a]					C [a]	C [a]
Amount of solvent (mole)	0·30	0·59					0·31 [c]	0·58
Amount of magnesium (g.-atom)	0·123	0·278					0·123	0·276
Reaction temperature	130°	130°					20—25°	130°
Time of addition of halide (min.)	29	45					20	70
Time of stirring (min.)	120	120					200	150
Amount of solvent added at end of reaction (mole)	0·298	0					0	0·29
Temperature at which 1-ml. portion was taken for analysis	20°	25°	25°	25°	25°	25°	20°	20°
Time after which aliquot portion was taken for analysis (hr.)	—	3	50	314	362	458	48	4
Base titre (ml. of 0·1N-H_2SO_4)	6·1	9·75	9·9	8·2	8·45	8·4	23·0 [d]	5·6
Yield of C–Mg material (%)	73	83·5	—	—	—	—	37	83·5
Halide titre (ml. of 0·1N-$AgNO_3$)	2·1	4·95	1·95	2·15	2·2	2·1	6·9 [d]	1·75
Base/halide ratio	2·9	2·0	5·1	3·8	3·8	4·0	3·3	3·2

Experiment no.	5	6	7	8
Organic halide	n-BuCl	n-BuCl	PhCl	PhCl
Amount of halide (mole)	0·080	0·080	0·084	0·082
Solvent	C [a]	T [b]	T [b]	T [b]
Amount of solvent (mole)	0·58	0·59	0·60	0·66
Amount of magnesium (g.-atom)	0·284	0·273	0·266 [f]	0·146
Reaction temperature	135°	130°	180—185°	180—185°
Time of addition of halide (min.)	35	50	20	25
Time of stirring (min.)	120	120	120	45
Amount of solvent added at end of reaction (mole)	0	0	1·51	1·07
Temperature at which 1-ml. portion was taken for analysis	25° / 25° / 25°	130° / 130°	180—185° / 23°	170° / 22° / 170°
Time after which aliquot portion was taken for analysis (hr.)	3 / 22 / 72	3·5 / 28·5	1 / 20	1 / 27 / 31·5
Base titre (ml. of 0·1N-H_2SO_4)	2·35 / 0·75 / 4·4 [d]	7·65 / 3·58	1·85 / 5·15 [d]	11·9 [d] / 5·8 [d] / 12·2 [d]
Yield of C–Mg material (%)	26·4 / — / —	85 / —	*ca.* 70 / —	— / — / *ca.* 75 [h]
Halide titre (ml. of 0·1N-$AgNO_3$)	1·15 / 0·15 / 0·3 [d]	2·0 / 0·7	0·6 / 1·6 [d]	2·1 [d] / 1·45 [d] / 2·2 [d]
Base/halide ratio	2·0 / 5·0 / 14·6	3·8 / 5·1	3·1 / 3·2	5·65 / 4·5 / 5·6

[a] C = Isopropylbenzene. [b] T = Tetrahydronaphthalene. Decahydronaphthalene, "Novasol" (Shell), and "Aladdin Pink paraffin" (purified with oleum and redistilled) also proved to be suitable solvents. [c] Diethyl ether (0·003 mole) was added. [d] Magnesium coarser than 40 mesh was used. [e] A similar experiment in which the proportion of magnesium was reduced to 4% of this figure (0·0114 g.-atom) gave no organomagnesium compounds. Instead, butylisopropylbenzene (52%), of unknown isomeric composition, was obtained, having b. p. 206—230°, n_D^{20} 1·4886 (Found: C, 88·7; H, 11·4. Calc. for $C_{13}H_{20}$: C, 88·5; H, 11·5%), together with n-octane (5%). Of the halogen in the n-butyl chloride, 75·5% appeared as free hydrogen chloride, and 7% as magnesium chloride. The total reaction period was 7 hr. [f] Magnesium was activated by heating it with *ca.* 2% by weight of iodine to *ca.* 300° in a stream of oxygen-free nitrogen. [g] 5-ml. aliquot parts were taken. [h] Carboxylation of a portion of the product gave benzoic acid, m. p. 120—121° and mixed m. p. 121°.

iodine was usually unnecessary, even with chlorides, but was occasionally resorted to in obstinate cases.

Reactions of n-Butyl Chloride, Bromide, and Iodide, and of Chlorobenzene with Magnesium in Hydrocarbon Media.—The procedures and principal results are summarised in Table 1.

Formation of $Bu^n_3Mg_2I$ *by Desolvation of Ethereal n-Butylmagnesium Iodide.*—n-Butylmagnesium iodide was prepared in the usual manner from n-butyl iodide (42·3 g., 0·23 mole) and magnesium turnings (6·2 g., 0·258 g.-atom) in diethyl ether (86 g.). The resulting solution was slowly sucked into isopropylbenzene (58 g.) which was refluxing under a reduced pressure of nitrogen at 130°. A white precipitate was formed immediately, and ether was driven off, through a Dufton column, with stirring. Distillation at 130° was continued until the refractive index of the distillate was that of isopropylbenzene (isopropylbenzene, n_D^{20} 1·4927; diethyl ether, n_D^{20} 1·3530). More (total 90 g.) isopropylbenzene was added at intervals during this process to maintain the liquid volume in the distillation flask.

After the mixture (volume 52 ml.) had been kept under nitrogen for 12 hr. at *ca.* 18°, the titres of the hydrolysis products of a 1-ml. aliquot part of the rather viscous clear supernatant liquid were 12·05 ml. of 0·1N-sulphuric acid, and 4·0 ml. of 0·1N-silver nitrate. Thus, the base/halide ratio was 3·0 After a further 72 hr., the corresponding figures were 12·4 ml., 4·0 ml., and 3·1. After the mixture had been heated for 4 hr. at 130°, and then set aside for 12 hr. at *ca.* 18°, the corresponding figures were 12·75 ml., 4·25 ml., and 3·0. In order to determine whether these figures referred to a saturated solution in contact with undissolved solute, isopropylbenzene (47 ml.) was then added, and the mixture stirred at 130° for 30 min. and then left for 12 hr. at *ca.* 18°, the analytical figures changing to 9·05 ml., 3·0 ml., and 3·0 respectively. Thus the base/halide ratio remained essentially constant, and the initial isopropylbenzene solution was saturated. The dissolution of solid phase after dilution gave an unsaturated solution, and did not modify the apparent empirical formula of the solute, *viz.*, $Bu^n_3Mg_2I$.

Reaction of Methyl Iodide with Magnesium.—Magnesium was activated as in Table 1, note *f*. The reaction conditions were similar to those in Table 1, experiment 1, except that the medium was a mixture of a petroleum fraction, b. p. 200—240° (30 ml.; from B.D.H.), and light petroleum, of b. p. 100—120° (8 ml.), the mixture refluxing at 130°. The product was insoluble and was brought into solution by the addition of ether. The yield of methylmagnesium compounds, estimated by the usual titration, was 10%. The use of isopropylbenzene as medium also gave an insoluble methylmagnesium product. Reactions were very difficult to initiate with unactivated magnesium, even by the subsequent addition of iodine.

Reaction of Ethyl Iodide with Magnesium.—The reaction conditions were similar to those in experiment 1, Table 1, except that magnesium turnings were employed and the medium was decahydronaphthalene. The product (7% yield) was very sparingly soluble, and the resulting saturated solution was 0·0035N at 20° with respect to C–Mg. Ethylmagnesium bromide with a base/halide ratio of 2·8 has been similarly obtained by Mr. E. T. Blues in *ca.* 6% yield.

Reaction of n-Propyl Bromide with Magnesium.—Under conditions similar to those in the previous experiment, the yield of n-propylmagnesium bromide was 15%. The saturated solution was 0·20N at 20°.

Reaction of Bromobenzene with Magnesium in Decahydronaphthalene.—Bromobenzene (*ca.* 1 ml. from 11·8 g.) was added to magnesium turnings (3·5 g.) in decahydronaphthalene (30 g.) at the reflux temperature (188°). Reaction commenced after 5 minutes' stirring, and the remainder of the bromobenzene was then added dropwise in 20 min. Refluxing was continued for a further 20 min., by which time the exothermic reaction had ceased. The product was sparingly soluble in the cold reaction medium, but dissolved on addition of ether. The yield of phenylmagnesium bromide was 95%.

The yield in a similar experiment performed at 170° was 40·5%.

The use of *m*- and *p*-bromotoluene as above at 188° gave yields of 87 and 64·5% respectively; but *o*-bromotoluene proved inert to magnesium under these conditions. Iodobenzene gave an 80·5% yield at 170° with a total reaction period of 90 min.

Polymerisation of Ethylene.—Phenylmagnesium chloride was prepared essentially as in experiment 7, Table 1, except that the solvent was a largely aliphatic petroleum fraction, b. p. 190—240°, obtained by treatment of " Aladdin Pink paraffin " with oleum. Benzene (300 ml.) was added to the cooled product. Titanium tetrachloride (14 ml. of a 10% solution in benzene) was added at intervals during 14 hr. After the addition of the first 2 ml., ethylene (dry, and

free from oxygen and carbon dioxide) was passed into the well-stirred dark brown suspension at 20°. Heat was evolved, and the temperature was maintained below 30° by cooling. After 15 hr., 36 g. of a polymer were obtained as a fine powder. The infrared spectrum was typical of a polyethylene. There was no significant chain-branching, as indicated by the absence of a peak at 7·25 μ. A small peak at 6·1 μ may have been attributable to the presence of phenyl residues.

Similar results were obtained when n-butylmagnesium chloride or iodide was used in place of phenylmagnesium chloride.

TABLE 2. *Variation with time of the viscosity and density at 25° of 0·26N-n-butylmagnesium iodide in isopropylbenzene after dilution from 0·52N.*

Time after dilution (hr.)	1	20	26	34	45	55	68
Time of flow (solution) (sec.)	1751	379	166	152	114	99	83
Time of flow (solvent) (sec.)	79	79	79	79	79	79	79
Density of solution	0·98	0·92	0·91	0·92	0·86	0·86	0·86
Reduced viscosity (100 ml. g.$^{-1}$)	6·53	1·19	0·52	0·49	0·40	0·55	0·31
Titre of 0·1N-acid * (ml.)	2·6	2·9	2·85	2·8	2·45	1·9	2·25
Base/halide ratio	3·0	3·4	3·3	3·3	3·5	3·4	3·4

* Ml. of 0·1N-hydrochloric acid required to neutralise the hydrolysis products of a 1-ml. sample.

Polymerisation of Propene.—Phenylmagnesium chloride was prepared as in experiment 8, Table 1, with chlorobenzene (11·5 g.), magnesium (7·5 g.), and tetrahydronaphthalene (80 g.). Dry benzene was then added, followed by titanium tetrachloride (1·2 g.), with vigorous stirring. Propene (dry, and free from oxygen and carbon dioxide) was passed slowly through the brown suspension for 14 hr. at 20—25°. The reaction was mildly exothermic. The resulting polymer was extracted successively with ether and light petroleum (b. p. 80—100°), to give a residue (20 g.) of isotactic polypropene (infrared spectrum).

Catalysts of lower reactivity but higher stereospecificity were obtained by substitution of titanium trichloride (brown or violet modifications) for the tetrachloride in the above experiment.

Ether was found to act as a catalyst poison.

Viscosity of a Solution of n-Butylmagnesium Iodide in Isopropylbenzene.—An Ostwald viscometer was adapted for use in an inert atmosphere, and all manipulations and measurements were made at 25° ± 0·01°. The solution was prepared essentially as in experiment 2, Table 1, and was left at 25° for 70 hr. A portion of the clear supernatant liquid was diluted from 0·52N to 0·26N with isopropylbenzene. Samples (vol. 9·91 ml.) used for a viscosity measurement were not returned to the main solution, but were removed for weighing to determine the density. The main results are given in Table 2. The erratic variation in the acid titres is unexplained; but we are inclined to attribute it to sampling errors, as similar solutions on other occasions gave no such variation. The base/halide ratios, which would be independent of sampling errors, were essentially constant. Density as well as viscosity decreased with time, and the values of both eventually became almost identical with those for the pure solvent.

Messrs. Albright and Wilson Limited are thanked for a maintenance grant (to G. F. C.).

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
READING.

[*Received, September 16th*, 1960.]

232. α-1,4-*Glucosans. Part XI.*[1] *The Absorption Spectra of Glycogen– and Amylopectin–Iodine Complexes.*

By A. R. Archibald, I. D. Fleming, A. Margaret Liddle, D. J. Manners, G. A. Mercer, and A. Wright.

The absorption spectra of the iodine complexes of a large number of starch-type polysaccharides have been measured. Amylopectins and glycogens show maximum absorption at *ca.* 540 and *ca.* 460 mμ respectively. This dissimilarity may be correlated with differences in type of iodine-binding arising from variations in the average length of the interior chains of the two polysaccharide-types. Mammalian glycogens are more iodophilic than invertebrate glycogens; this fact cannot at present be related to known structural features.

Addition of ammonium sulphate and other salts to a polysaccharide–iodine solution causes a marked increase in the iodine-staining power of glycogen, but only a small increase with amylopectin. Under these conditions, the position of maximum absorption is approximately related to the degree of branching in the polysaccharide.

The action of branching or debranching enzymes, which catalyse the synthesis or hydrolysis of α-1,6-glucosidic inter-chain linkages in starch-type polysaccharides may be followed by measurement of changes in the iodine-staining power of the substrate. For example, the activity of liver branching enzyme is determined from the decrease in optical density at 570 mμ of an amylopectin–iodine solution,[2] whilst R-enzyme is assayed from the increase in " blue value " of amylopectin β-dextrin.[3] There is some evidence [4,5] that the iodine-staining power of amylose is related to the average chain length ($\overline{CL}$) or degree of polymerisation ($\overline{DP}$) provided that the amylose molecules do not exceed a certain critical size, although there is no apparent agreement on the actual value of this. However, information on the possible relation between the absorption spectrum of a glycogen– or amylopectin–iodine complex and the degree of branching in the polysaccharide is not available, and we now report such an investigation. A preliminary account of part of this work has been given.[6]

In previous papers of this Series,[1,7,8] the $\overline{CL}$ and β-amylolysis limit of a large number of glycogens and amylopectins, have been reported; from these data, the relative lengths of the exterior and the interior chains have been calculated. The absorption spectra of the iodine complexes of these polysaccharides have now been determined, in conditions similar to those used by Peat and his co-workers [9] in their iodine-staining studies of the action of R-enzyme on glycogen, *i.e.*, the light absorption in the range 400—700 mμ of a solution containing 0·01% of polysaccharide and 0·02% of iodine in 0·2% aqueous potassium iodide was measured on a Unicam S.P. 500 or S.P. 600 spectrophotometer against an iodine–iodide reference solution. Typical curves are shown in Fig. 1; effects due to light absorption by the polysaccharide alone are negligible under these conditions. With glycogens, a wide absorption peak covering 20—30 mμ was frequently obtained, and the $\lambda_{max.}$ quoted represent the mid-points; with amylopectins, a sharper peak was observed and the $\lambda_{max.}$

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[5] Swanson, *J. Biol. Chem.*, 1948, **172**, 825; Bailey, Whelan, and Peat, *J.*, 1950, 3692; Kerr, Cleveland, and Katzbeck, *J. Amer. Chem. Soc.*, 1951, **73**, 3916.
[6] Archibald, Manners, and Wright, *Biochem. J.*, 1960, **75**, 10P; Liddle, Ph.D. Thesis, Edinburgh 1956; Archibald, Ph.D. Thesis, Edinburgh 1958.
[7] Fleming, Hirst, and Manners, *J.*, 1956, 2831.
[8] Manners and Khin Maung, *J.*, 1955, 867; Manners and Archibald, *J.*, 1957, 2205; Liddle and Manners, *J.*, 1957, 3432.
[9] Peat, Whelan, Hobson, and Thomas, *J.*, 1954, 4440.

values are significant to ± 5 mμ. From the above curves $\lambda_{max.}$ and $E_{max.}$ (the extinction or absorption value at this wavelength) were noted for each polysaccharide, and the results are recorded in Table 1. Control experiments showed that the $\lambda_{max.}$ values were unaffected by variation in the polysaccharide : iodine ratio; the figures as quoted for $E_{max.}$ values are considered to be significant, although slight variation was observed (*e.g.*, in triplicate solutions Floridean starch II had $E_{max.}$ 0·68, 0·67, and 0·72 at 530 mμ).

The general results indicate a marked difference in the absorption spectra of the iodine complexes of amylopectins and glycogens. The former complexes show much stronger absorption ($\lambda_{max.}$ 530—550 mμ, $E_{max.}$ 0·8—1·2) than those of glycogen ($\lambda_{max.}$ 420—490 mμ, $E_{max.}$ 0·1—0·4) even though the $\overline{CL}$ values of some amylopectins (*ca.* 20) are not greatly different from those of certain glycogens. This is especially true of malt amylopectin and horse muscle glycogen (Fig. 1).

The iodine absorption spectra of individual glycogens vary considerably and, for aqueous solutions, they appear to depend upon the biological source and not on the average

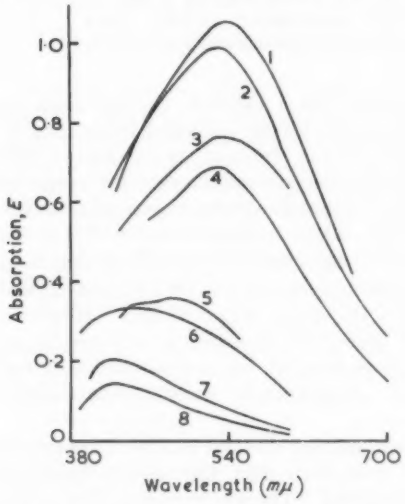


FIG. 1. *Light-absorption curves of iodine-stained polysaccharides.*

1, Waxy sorghum starch; 2, waxy maize starch; 3, malt amylopectin; 4, Floridean starch; 5, horse muscle glycogen; 6, rabbit liver glycogen; 7, skate liver glycogen; 8, *Mytilis edulis* glycogen.

or exterior chain length. There is no correlation between the $\lambda_{max.}$, $E_{max.}$, or extinction at a particular wavelength (*e.g.*, 460 mμ) and the branching characteristics. It follows that increases in the absorption spectra of the iodine complexes of liver glycogen isolated from animals in different metabolic conditions [10] are not necessarily due to changes in molecular structure. Previous observations [11] that fish and invertebrate glycogens give yellow-brown stains with iodine whilst mammalian samples give red-brown colours have been confirmed. In general, the iodine-staining power increased in the order, glycogen β-limit dextrin, invertebrate glycogen, mammalian liver glycogen, and mammalian muscle glycogen. This variation of iodine-staining power with biological source is an important factor in iodine-staining methods for the determination of glycogen, and separate calibration curves are suggested for glycogen samples from different species.[12]

The iodine-staining of the Floridean starches and sweet-corn polysaccharides is of special interest. The algal polysaccharides resemble typical glycogens rather than amylopectins with regard to degree of branching,[7] and yet give appreciably more intense iodine-stains than do the animal polysaccharides. A sample of Floridean starch examined by

[10] Chapman, Fells, and Chaikoff, *Experientia*, 1955, **11**, 283.
[11] Bell and Kosterlitz, *Biochem. J.*, 1935, **29**, 2027; Bell, *ibid.*, 1935, **30**, 2144.
[12] Van der Vies, *Biochem. J.*, 1954, **57**, 410.

TABLE 1. *Iodine-staining properties of polysaccharides.*

Polysaccharide	$\lambda_{max.}$ (mμ)	$E_{max.}$	$\overline{CL}$ *	$\overline{ECL}$ †	$\overline{ICL}$ †
Glycogens:					
Arenicola	420	0·2	11 [e]	7—8	2—3
Ascaris lumbricoides	435	0·2	12 [a]	8	3
Cardium	420	0·1	8 [e]	3—4	3—4
Cat liver IV	465	0·3	13 [e]	9—10	2—3
Cock liver	440	0·1	13 [e]	7—8	4—5
Fœtal pig liver	440	0·5	11 [e]	8	2
Helix pomatia II	425	0·1	7 [a]	4	2
Horse muscle	460	0·3	11 [a]	7	3
Human liver I	460	0·2	14 [b]	9	4
II	430	0·05	6 [b]	2	3
Mytilus edulis I	435	0·1	12 [a]	7—8	3—4
II	440	0·2	16 [a]	10—11	4—5
IV	450	0·1	12 [e]	8—9	2—3
VII	420	0·2	13 [e]	8—9	3—4
VIII	420	0·2	13 [e]	8—9	3—4
IX	430	0·2	10 [e]	7—8	1—2
X	420	0·2	14 [e]	8—9	4—5
Oyster	440	0·2	10 [e]	6—7	2—3
Rabbit liver I	455	0·2	13 [e]	5—6	6—7
IV	460	0·3	13 [e]	8—9	3—4
V	450	0·3	14 [e]	9—10	3—4
VIII	460	0·2	13 [e]	9	3
IX	485	0·4	13 [e]	9	3
X	475	0·3	12 [e]	8—9	2—3
Rabbit muscle I	490	0·4	12 [a]	8	3
III	490	0·3	13 [e]	8—9	3—4
Skate liver	420	0·2	13 [e]	8—9	3—4
Trichomonas gallinae II	440	0·3	13 [8]	8—9	3—4
Yeast (brewer's)	430	0·3	13 [8]	8	4
Amylopectins:					
Potato I (King Edward)	540	1·3	23 [e]	14—15	7—8
II (Great Scot)	555	1·2	24 [d]	17	6
Protozoal	530	1·3	22 [e]	15—16	5—6
Waxy maize starch I	530	1·0	22 [e]	14—15	6—7
II	530	0·9	21 [8]	15	5
Waxy sorghum starch II	535	1·0	22	15	6
Other polysaccharides:					
Ascaris glycogen β-dextrin	430	0·1	6—7	2—3	3
Fœtal sheep liver glycogen β-dextrin	430	0·1	6—7	2—3	3
Floridean starch I	500	0·8	9 [7]	6—7	1—2
II	530	0·7	12 [7]	7	4
III	530	0·6	13 [7]	7—8	4—5
Helix glycogen β-dextrin	430	0·03	4—5	1—2	2
Rabbit liver glycogen dextrin	460	0·3	9	5	3
Waxy maize starch β-dextrin	530	0·9	10	2—3	6—7
Waxy sorghum starch β-dextrin	540	0·8	12	2—3	8—9
Zea mays *polysaccharides*:					
Phytoglycogen A	450	0·2	13 [14]	9	3
B	430	0·2	7 [14]	5	1
Fraction 55—60	480	0·2	10 [14]	—	—
60—65	450	0·2	11 [14]	—	—
65—70	445	0·1	10 [14]	—	—

* Average chain length, determined by periodate oxidation (superscript numbers refer to the previous results and the superscript letters to the following references: *a*, Bell and Manners, *J.*, 1952, 3641; *b*, Calderbank, Kent, Lorber, Manners, and Wright, *Biochem. J.*, 1960, **74**, 223; *c*, Manners and Wright, unpublished work; *d*, Fleming and Mercer, unpublished work; *e*, Liddle and Manners, *J.*, 1957, 3432).

† $\overline{ECL}$, exterior chain length, *i.e.*, no. of glucose residues removed by β-amylase + 2·5; $\overline{ICL}$, interior chain length, *i.e.*, $\overline{CL} - \overline{ECL} - 1$.

Peat, Turvey, and Evans [13] which had $\overline{CL}$ 15 also showed $\lambda_{max.}$ 530 mμ. The water-soluble polysaccharides from *Zea mays* are structurally indistinguishable from animal glycogens,[14] and the data in Table 1 are in accord with this finding.

In contrast to the glycogens, amylopectins from various plant and protozoal starches showed similar $\lambda_{max.}$ values; there was some variation in the extinction at 680 mμ and this is attributed to the presence of small amounts of amylose as impurity in the amylopectin samples. For example, although waxy maize starch is normally considered to be free from amylose, potentiometric titration [15] has indicated the presence of 1·4% of linear polysaccharide in sample I. However, control experiments have shown that the presence of even 5% of amylose impurity does not appreciably affect the position of $\lambda_{max.}$.

The iodine-staining properties of glycogen and amylopectin show a more marked difference after β-amylolysis. With glycogen, both $\lambda_{max.}$ and $E_{max.}$ are decreased, whereas amylopectin β-dextrin has the same $\lambda_{max.}$ as the original polysaccharides. It is clear

FIG. 2. *Relation between interior chain length of a polysaccharide and* $\lambda_{max.}$ *of the iodine complex.* ● *and* ○ *represent glycogen and amylopectin respectively.*

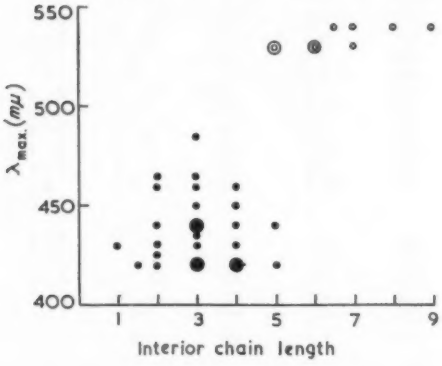
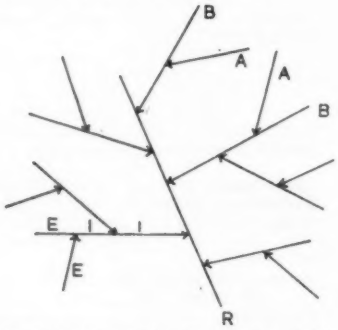


FIG. 3. *Multiply-branched structure for amylopectin and glycogen.*



R, *Reducing-group*; E, *exterior chain*; I, *interior chain*; A, A-*chain*; B, B-*chain*.

that in amylopectin, the $\lambda_{max.}$ of the iodine complex is not related to the length of the exterior chains. In contrast, there is evidence [15] that the iodine-binding power of branched α-1,4-glucosans, as determined by potentiometric titration, increases with the length of the exterior chains.

TABLE 2. *Calculated * lengths of A- and B-chains.*

	$\overline{CL}$	β-Amylolysis limit (%)	Average lengths A-chain	B-chain
Amylopectin	20 †	57 †	14	26
Glycogen	12 †	45 †	8	16

* The exterior A- and B-chain stubs in a β-dextrin are assumed to contain 2—3 glucose residues.
† Typical experimental results.

The above results indicate that the nature of the iodine-binding in glycogen and in amylopectin is different. Higginbotham [16] has suggested that amylopectin binds iodine partly by the adsorption of iodine molecules or tri-iodide ions, and partly by a mechanism in which iodine molecules are arranged endwise and axially inside a series of helices of

[13] Peat, Turvey, and Evans, *J.*, 1959, 3341.
[14] Peat, Whelan, and Turvey, *J.*, 1956, 2317.
[15] Anderson and Greenwood, *J.*, 1955, 3016.
[16] Higginbotham, *Shirley Inst. Mem.*, 1949, **23**, 171.

α-1,4-linked glucose residues. Each coil of the helix is believed to contain six glucose residues and one iodine molecule.[4] The smallest amylose-type molecule which gives a colour with iodine probably contains *ca.* 18 glucose residues,[17] *i.e.*, a sequence of three helical coils is required.

One possible explanation for the difference in the iodine-staining properties of amylopectin and glycogen is the characteristic difference in the average length of the interior chains (see Fig. 2) and hence of the B-chains.* By definition, the molecules contain an equal number of exterior and interior chains, and if we assume that amylopectin and glycogen comprise an equal number of A- and B-chains,[18] each A-chain * represents an exterior chain, whilst every B-chain contains one exterior and two interior sections (see Fig. 3). Calculation (Table 2) shows that with amylopectin a considerable proportion of the B-chains would be of a suitable length to assume a helical configuration. In contrast, only a small proportion of the B-chains in glycogen would exceed $\overline{CL}$ 18. It has been suggested that the presence of branch points would interfere with complex formation;[4] however, inspection of models[19] of

TABLE 3. *Iodine-staining properties of glycogens determined by Schlamowitz's method.*[22]

Glycogen	$\lambda_{max.}$ (mμ)	$E_{max.}$	$\overline{CL}$ *	$\overline{ECL}$ *	$\overline{ICL}$ *
Mytilus edulis IX	500	0·5	10 *	7—8	1—2
Rabbit muscle I	520	0·3	12 *	8	3
Rabbit liver X	500	0·6	12 [f]	8—9	2—3
Tetrahymena pyriformis II	505	0·5	14 [f]	9	4
Trichomonas foetus	505	0·5	15 [f]	11—12	2—3
Trichomonas gallinae II	495	0·6	13 [f]	8—9	3—4
Zea mays					
Phytoglycogen A	550	0·5	13 [14]	—	—
B	530	0·2	7 [14]	—	—

* See Footnotes to Table 1. [f] Manners and Archibald, *J.*, 1957, 2205.

glucose residues in a helix shows that the primary 6-alcohol groups are situated on the outer surfaces of the helix so that the attachment of side-chains to a B-chain should not necessarily affect the interior of the helix.

An additional factor concerns the ability of iodine molecules (size approx 8 Å) and the even larger tri-iodide ion to penetrate the interior of the compact glycogen molecule, as compared with the more open interior of an amylopectin molecule. This is illustrated by the fact that amylopectin β-dextrin, which has the same degree of branching as a normal glycogen, still retains the characteristic amylopectin-type absorption with $\lambda_{max.}$ *ca.* 535 mμ.

The spectral differences between the iodine complexes may, therefore, be related to differences in the average distance between branch points in the interior of the molecules. Since it is now known that glycogen and amylopectin have similar degrees of multiple branching (*i.e.*, the ratios of A-chains to B-chains are similar),[18] this property is not a controlling factor (cf. ref. 15).

It is concluded that, under the above experimental conditions, the absorption spectra of polysaccharide–iodine complexes cannot be directly related to the proportion of α-1,6-glucosidic inter-chain linkages. The use of iodine-staining methods for the study of branching or debranching enzymes cannot therefore give quantitative information on changes in the proportion and distribution of 1,6-linkages in the substrate. Nevertheless, qualitative information can be conveniently obtained. In addition, determination of the $\lambda_{max.}$ of a polysaccharide–iodine complex, together with examination of other properties,

* An A-chain (side-chain) is linked to the molecule only by the reducing group, whilst B-chains (main-chains) which are similarly linked, also have other chains attached to them.

[17] Thoma and French, *J. Amer. Chem. Soc.*, 1960, **82**, 4144.
[18] Peat, Whelan, and Thomas, *J.*, 1956, 3025; Liddle and Manners, *J.*, 1957, 4708.
[19] Cf. Greenwood and Rossotti, *J. Polymer Sci.*, 1958, **27**, 481.

FIG. 4. *Effect of ammonium sulphate on the iodine complex of* Trichomonas gallinae *glycogen. Curves* 1 *and* 2 *were measured for half-saturated and quarter-saturated ammonium sulphate solution. Curve* 3 *shows the spectra in water.*

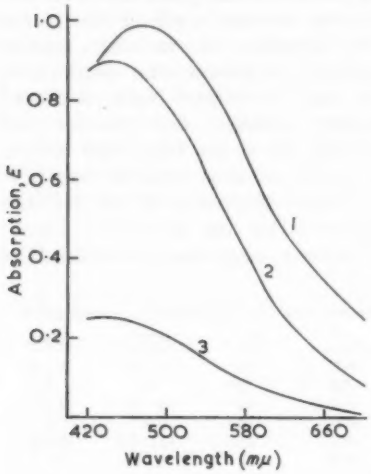


FIG. 5. *Relation between the average chain length of an amylopectin-glycogen type polysaccharide and* $\lambda_{max.}$ *of the iodine complex in half-saturated ammonium sulphate solution.*

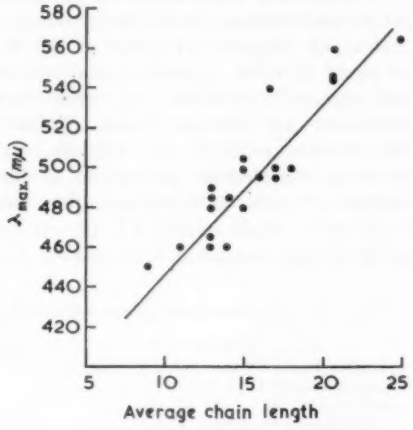


TABLE 4. *Effect of half-saturated ammonium sulphate on the absorption spectra of polysaccharide–iodine complexes.*

Polysaccharide	Water $\lambda_{max.}$ (mμ)	Water $E_{max.}$	NH_4 sulphate $\lambda_{max.}$ (mμ)	NH_4 sulphate $E_{max.}$	$\overline{CL}$ *	$\overline{ECL}$ *	$\overline{ICL}$ *
Glycogens:							
Fœtal sheep liver	450	0·3	485	0·6	13 [e]	9	3
Horse muscle	490	0·3	495	0·6	16—17 [1]	10—11	5
Human kidney	445	0·2	460	0·6	14 [b]	9	4
Human muscle	445	0·1	460	0·6 †	11 [e]	7	3
Mytilus edulis V	420	0·2	450	0·8	9 [f]	6	2
VI	445	0·1	480	1·0	13 [f]	8—9	3—4
Ox muscle	480	0·3	505	0·7 †	15 [1]	10	4
Rabbit liver VI	465	0·3	500	1·1	18 [e]	12	5
XII	460	0·2	500	1·0	17 [e]	9—10	6—7
XIII	470	0·3	480	1·0	15 [e]	9—10	4—5
Rabbit muscle II	460	0·2	490	0·9	11 [e]	6—7	3—4
Tetrahymena pyriformis I	445	0·3	465	0·9	13 [g]	8—9	3—4
II	440	0·3	485	0·9	14 [f]	9	4
Trichomonas foetus	445	0·4	500	1·1	15 [h]	11—12	2—3
Trichomonas gallinae II	440	0·3	480	1·0	13 [f]	8—9	3—4
Amylopectins:							
Malted barley	535	0·9	540	1·1	18 [i]	10—11	6—7
Potato III (Kerr's Pink)	540	1·1	545	0·7 †	22 [e]	16	5
IV (Epicure)	550	1·3	545	0·7 †	24 [j]	16	7
Protozoal (*Chilomonas paramecium*)	540	1·2	545	1·4	22 [k]	15—16	5—6
Waxy maize starch IV	530	1·1	560	1·6	22 [e]	15	6
Waxy sorghum starch I	540	1·1	560	1·2	25 [e]	15—16	8—9
β-Dextrins:							
Fœtal sheep liver glycogen	425	0·1	415	0·4 †	6—7	2—3	3
Mytilus edulis VI	420	0·03	420	0·3 †	7	2—3	3—4
Rabbit liver II	420	0·2	425	0·5 †	9	2—3	5—6
Waxy maize starch I	535	0·9	535	0·5 †	10	2—3	6—7

* See Footnotes to Table 1; additional references are, *g*, Manners and Ryley, *Biochem. J.*, 1952, **52**, 480; *h*, *idem*, *ibid.*, 1956, **59**, 369; *i*, Aspinall, Hirst, and McArthur, *J.*, 1955, 3075; *j*, Banks and Greenwood, unpublished work; *k*, Archibald, Hirst, Manners, and Ryley, *J.*, 1960, 556.

† Polysaccharide concentration 0·005%.

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may enable a distinction to be made between a " glycogen "- and an " amylopectin "-type polysaccharide. The results obtained so far are in good agreement with those from potentiometric iodine titrations.[15]

Effect of Ammonium Sulphate on Polysaccharide–Iodine Colorations.—The exact colour of a polysaccharide–iodine solution depends upon many factors,[20] but at constant temperature and with a constant concentration of reactants it may be increased by the presence of various salts, especially ammonium sulphate.[21]

Schlamowitz examined the absorption spectra of several glycogen–iodine complexes in 50% saturated ammonium sulphate under conditions in which a large excess of glycogen was present.[22] For many glycogens, $\lambda_{max.}$ was *ca.* 496 mμ, and was independent of $\overline{CL}$, although $E_{max.}$ appeared to be roughly proportional to the $\overline{CL}$ value. The significance of these results is lessened by the fact that $\overline{CL}$ values were obtained [22] by a periodate oxidation method [23] which was originally applied to amylopectins. With glycogens, this method does not give satisfactory results (cf. Manners and Archibald [8]). Using Schlamowitz's conditions we measured $\lambda_{max.}$ and $E_{max.}$ for various glycogens, but were unable to find any relation between these properties and the $\overline{CL}$ (see Table 3).

In contrast to these results, addition of ammonium sulphate to 25% or 50% saturation in glycogen–iodine solutions, prepared as in Table 1, caused a marked increase in iodine-staining (Fig. 4, Table 4); *e.g.*, $E_{max.}$ values increased from 0·1 to 0·4 to the range 0·6—1·1. However, the solutions in 50% saturated ammonium sulphate became turbid, and a glycogen–iodine complex was slowly precipitated. (In one experiment, $E_{max.}$ fell from 0·87 to 0·82 within 15 minutes.) $E_{max.}$ values had, therefore, to be measured immediately after mixing. In later experiments, the stability of the solutions was increased by halving the glycogen concentration; this also halved $E_{max.}$ but did not affect $\lambda_{max.}$. In water or 25% ammonium sulphate solution, the glycogen–iodine solutions were clear and stable.

Glycogen β-dextrins were also examined; there was no appreciable change in $\lambda_{max.}$, although $E_{max.}$ increased (Table 4).

With amylopectin–iodine solutions, 50% ammonium sulphate caused only a slight increase in coloration; this was accounted for by an increase in $E_{max.}$ (from 0·9—1·2 to 1·1—1·6) rather than a change in $\lambda_{max.}$. Amylopectin β-dextrin behaved similarly.

Inspection of the results in Table 4 suggests that, with amylopectin and glycogen, $\lambda_{max.}$ is approximately related to the degree of branching; a correlation diagram is shown in Fig. 5. Since the length of the exterior chains is dependent on $\overline{CL}$, it follows that $\lambda_{max.}$ is also related to the exterior chain length. It may be possible to deduce $\overline{CL}$ values from measurements of $\lambda_{max.}$ under these conditions. By the method of least squares, with $\lambda_{max.}$ as the independent variable, these properties are related by the equation: $\overline{CL} = 16 + 0{\cdot}114\ (\lambda_{max.} - 500)$. The standard error in $\overline{CL}$ would be *ca.* 1·6 glucose residues. (We are indebted to Mr. A. G. Cock, Poultry Research Centre, Edinburgh, for this statistical analysis.)

It has been suggested [22] that ammonium sulphate facilitates iodine-complex formation by dehydration, providing a more hydrophobic environment for the iodine molecules. It is possible that a few of the longer B-chains in a glycogen molecule can, under these conditions, bind a limited amount of iodine by the helical mechanism rather than by adsorption.

Other salts, *e.g.*, magnesium sulphate, sodium sulphate, and sodium nitrate also increase the intensity of a glycogen–iodine coloration, but the effect is less than with ammonium sulphate.

[20] Morris, *J. Biol. Chem.*, 1946, **166**, 199.
[21] Sumner and Somers, *Arch. Biochem.*, 1944, **4**, 7.
[22] Schlamowitz, *J. Biol. Chem.*, 1951, **190**, 519.
[23] Potter and Hassid, *J. Amer. Chem. Soc.*, 1948, **70**, 3488.

Experimental

Most of the polysaccharide samples have been described elsewhere. We are grateful to Dr. G. O. Aspinall for the malt amylopectin, Dr. C. T. Greenwood for potato amylopectin IV, and Dr. J. R. Turvey for the *Zea mays* polysaccharides. The polysaccharide concentrations are based on the glucose content determined after acid-hydrolysis.

Effect of Polysaccharide Concentration on $\lambda_{max.}$.—Solutions containing severally 2·5, 1·5, and 1·0 mg. of horse muscle glycogen, 2·5 ml. of a 0·2% solution of iodine in 2·0% aqueous potassium iodide, and 1 drop of 3N-hydrochloric acid in a total volume of 25 ml. were prepared. In all three solutions, $\lambda_{max.}$ was 480 ± 5 mμ; $E_{max.}$ values were 0·25, 0·15, and 0·11 respectively.

Effect of Amylose as Impurity on Amylopectin–Iodine Solution.—Solutions containing potato amylopectin and 0, 5, or 10% w/w of potato amylose were prepared. The respective $\lambda_{max.}$ values were 555, 560, and 570 mμ, and $E_{max.}$ values 0·26, 0·28, and 0·33. The absorption of the amylose–iodine complexes alone was also measured. The effect was found to be additive.

Effect of β-Amylolysis on the Iodine-staining Power.—Digests containing rabbit liver VII glycogen and potato amylopectin (*ca.* 50 mg.) were incubated at pH 4·6 and 35° with barley β-amylase (2500 units) in a total volume of 50 ml. Samples (10 ml.) were removed at intervals, and heated to inactivate the enzyme. The conversion into maltose was determined, and equal *weights* of polysaccharide (≡ 2·3 mg.) stained with iodine and water or (≡ 1·15 mg.) stained with iodine and ammonium sulphate solution. Results are tabulated. If equal *volumes* of polysaccharide–β-amylase mixture are stained with iodine, $E_{max.}$ decreases as the percentage conversion into maltose increases.

Time of incubation (hr.)	β-Amylolysis limit (%)	Water		Aq. $(NH_4)_2SO_4$	
		$\lambda_{max.}$ (mμ)	$E_{max.}$	$\lambda_{max.}$ (mμ)	$E_{max.}$
		Potato amylopectin			
0	0	540	1·1	540	0·7
0·5	61	540	1·5	540	0·6
2·0	64	540	1·6	545	0·6
29	65	545	—	540	—
		Rabbit liver glycogen			
0	0	450	0·3	490	0·5
0·5	41	425	0·2	440	0·3
2·0	51	410	0·2	425	0·4
29	55	430	0·1	425	0·4

Effect of Various Salts on the Iodine-staining Power.—Rabbit muscle III or *Mytilus edulis* VI glycogen (final concentration 0·005%) was stained with iodine in the presence of half-saturated solutions of various salts, with the tabulated results.

	Rabbit muscle glycogen		*Mytilus edulis* glycogen			Rabbit muscle glycogen		*Mytilus edulis* glycogen	
Conditions	$\lambda_{max.}$ (mμ)	$E_{max.}$	$\lambda_{max.}$ (mμ)	$E_{max.}$	Conditions	$\lambda_{max.}$ (mμ)	$E_{max.}$	$\lambda_{max.}$ (mμ)	E_{max}
Water	495	0·30	445	0·12	K nitrate	470	0·34	—	—
NH_4 sulphate	490	0·96	455	0·73	K sulphate ...	485	0·31	445	0·25
NH_4 nitrate ...	505	0·22	445	0·13	Na nitrate ...	—	—	450	0·35
Ca chloride ...	—	—	430	0·27	Na sulphate ...	485	0·35	445	0·29
Mg sulphate ...	495	0·50	440	0·51					

The authors are indebted to Professor E. L. Hirst, C.B.E., F.R.S., for his interest and encouragement, to Mr. R. A. A. Hurst, Dr. I. G. Jones and Miss K. Shannon for assistance with preliminary experiments, to the Department of Scientific and Industrial Research for maintenance allowances (to A. R. A., I. D. F., A. M. L., and A. W.), and to Cerebos Ltd. for the award of a research scholarship (to G. M.).

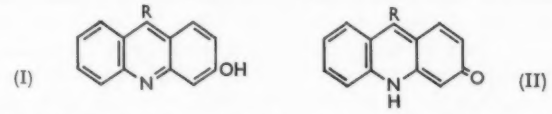
Department of Chemistry, University of Edinburgh. [*Received, August 26th,* 1960.]

233. *Tautomerism in the Solid State. Part II.**

By Neil Campbell and A. G. Cairns-Smith.

The colour changes undergone by 3-hydroxy-9-phenylacridine have been examined and are held to be related to lactim–lactam tautomerism.

Kehrmann and Matuzinsky [1] obtained 3-hydroxy-9-phenylacridine as yellow needles, m. p. 264°, which were converted instantaneously by pressing or rubbing into a red powder, m. p. 135°, and the authors suggested that this is the result of tautomeric change from the lactim (I; R = Ph) to the lactam form (II; R = Ph). It was reported that the compound crystallised from cold benzene in red crystals and from hot benzene in the yellow



(I) (II)

form, and that the yellow form on storage became red and could be obtained by heating the red form above 135°. It was concluded that the red form is stable at room temperature and the yellow above 135°.

We have investigated these changes and our observations and conclusions differ materially from those of Kehrmann and Matuzinsky, although we confirm their suggestion that mild compression or friction can induce tautomeric changes in the solid state.

Comparison of the spectrum of 3-hydroxy-9-phenylacridine in various solvents with the spectra of the *O*- and the *N*-methyl ether shows that the compound exists in solution as a tautomeric equilibrium between the yellow lactim and the red lactam (I and II; R = Ph). The spectrum of the hydroxy-compound in contrast to those of the ethers varies considerably with change of solvent. In cyclohexane the compound exists as the lactim form with an ultraviolet spectrum similar to that of its *O*-methyl ether (Fig. 1), and in 20% aqueous ethanol as the lactam with a spectrum resembling that of the *N*-methyl ether (Fig. 2). In absolute ethanol the maxima of both forms are clearly visible (Fig. 3). These observations are similar to those made on 3-hydroxyacridine [2] (I and II; R = H) and certain hydroxyphenazines such as 2-hydroxy-1,3,4-trimethylphenazine.[3] Grinding these substances, however, effects no colour change. Incidentally, since the spectra of 3-hydroxy- and 3-hydroxy-9-phenyl-acridine are similar, the phenyl group in the latter cannot be coplanar with the acridine ring.[4]

At a fairly high temperature and under reduced pressure 3-hydroxy-9-phenylacridine sublimes and a fine-grained red film on a cooled silica plate was thus obtained. Heating the plate for one minute at 140° produced a corresponding film of the yellow form and, provided the change was sufficiently rapid, the grain size was still below the limits of a low-powered microscope. From these films qualitative spectra were obtained in which absorption maxima can be distinguished clearly. The curves obtained from the red film are shown in Fig. 4, curve (A) being obtained before and curve (B) after heating at 140°. The following points may be noted. The transition from the red to the yellow form is accompanied by the disappearance of the long-wave lactam absorption band and an inflexion at 290 mμ also in the position of a band characteristic of the lactam form. Both solid forms show a maximum between 358 and 360 mμ along with an inflexion or smaller maximum at 345 mμ, but this conveys little information since a feature of this type is observed both in lactim and lactam absorptions (Fig. 1 and 2). In both curves there is

* Part I, *J.*, 1961, 182.

[1] Kehrmann and Matuzinsky, *Ber.*, 1912, **45**, 3498; *Annalen*, 1917, **414**, 182.
[2] Albert and Short, *J.*, 1945, 760.
[3] John, *Z. angew. Chem.*, 1947, **59**, 188.
[4] Braude, Fawcett, and Webb, *J.*, 1954, 1049.

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a maximum at 410 mμ, the intensity of which increases when the red form is changed to the yellow. This is indicative of the lactim form since the *O*-methyl ether absorbs in the 380—400 mμ region whereas the *N*-methyl ether has an absorption minimum in this region. It may be concluded from these results that the yellow form of 3-hydroxy-9-phenylacridine exists mainly or entirely in the lactim form, and the red form contains both the lactim and the lactam form. These conclusions are emphasised by the absorption curve

Ultraviolet absorption spectra.

FIG. 1. (A) *3-Hydroxy-9-phenylacridine (qualitative), and* (B) *O-methyl ether; in cyclohexane.*

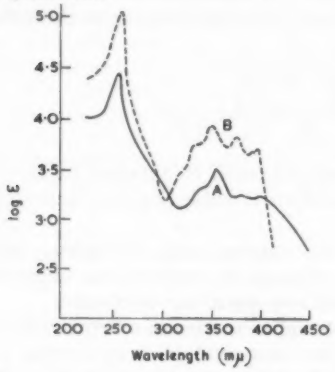


FIG. 2. (A) *3-Hydroxy-9-phenylacridine in 20% ethanol;* (B) *N-methyl derivative in n-hexane.*

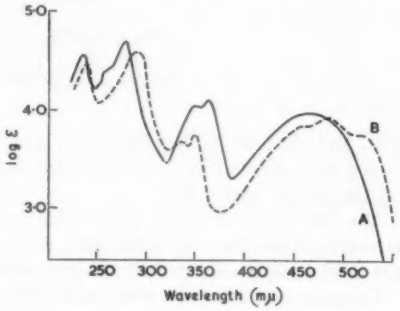


FIG. 3. (A) *3-Hydroxy-9-phenylacridine in absolute ethanol;* (B) *solid red form (qualitative).*

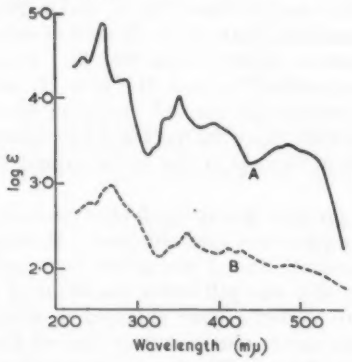
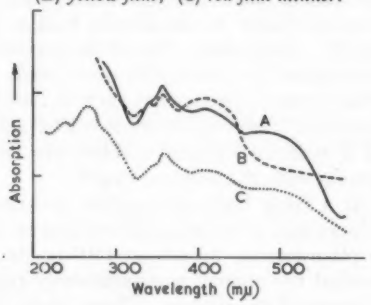


FIG. 4. *Qualitative spectra:* (A) *red film;* (B) *yellow film;* (C) *red film thinner.*



obtained from a thinner film of the red form (C) (Fig. 4) which shows a strong absorption at 268 mμ corresponding to lactim absorption at 260 mμ, and another at 240 mμ comparable to that of the lactam absorption of the *N*-methyl compound at 240 mμ in cyclohexane and 238 mμ in absolute ethanol. Also in harmony with our conclusions is the similarity of the spectrum of the red film and the spectrum of the hydroxyphenylacridine in absolute ethanol (Fig. 3).

It might be objected that the red sublimate is not the same substance as that obtained by grinding the yellow hydroxyphenylacridine. That the two are the same was shown by grinding the compound on to silica plates and examining the spectrum. The particle size in these films was much greater and the resultant scattering produced a pronounced levelling out of the spectrum. Nevertheless the " mixed " nature of the spectrum was

shown by its similarity to that of the sublimed red film. It therefore seems clear that the colour change which occurs when the yellow crystals of 3-hydroxy-9-phenylacridine are pressed or rubbed is due to tautomerism; that the mobile hydrogen atom is attached to the oxygen atom in the yellow solid; and that in the red solid a substantial proportion of the hydrogen atoms are attached to the nitrogen.

Further insight into the colour change was obtained from *X*-ray powder photographs which showed that the yellow form is crystalline and the red form is almost amorphous. Only one faint line could be seen in the photograph of the red form and this corresponded to a particularly intense line in the photograph of the yellow form. There can be little doubt therefore that grinding the yellow crystals of 2-hydroxy-5-phenylacridine results in tautomerisation and lattice disintegration.

The amorphous nature of the red compound implies that the red form should be metastable at all temperatures below the melting point of the compound and this is contrary to Kehrmann's view that the red substance is the pure lactam and is stable at room temperature. This discrepancy has to some extent been overcome by a re-investigation of Kehrmann's observations. We were unable to obtain any evidence that the yellow form becomes red when kept *in the dark*, nor were we able to obtain clean-cut red crystals from cold benzene solutions. We found, however, that the yellow form slowly becomes orange when kept *in light* and that by allowing a benzene solution to evaporate at room temperature a mixture of yellow crystals and red supercooled liquid is deposited. The supercooled liquid crystallises only very slowly, but the effect may be accelerated by heating and proceeds fairly rapidly at 130—140°. In addition to the yellow crystals and the red glass, slow evaporation may indeed produce " brick-red crystals with a metallic sheen," but one end of such a crystal may conform to this description while the other is pure yellow. Kehrmann's " red crystals " are in fact artefacts of yellow crystals covered by a layer of red supercooled liquid. There is thus no evidence of the existence of a crystalline, red modification of 3-hydroxy-9-phenylacridine.

The temperature, 135°, reported by Kehrmann as a transition temperature has little significance. Even at 100° the red form is converted into the yellow in two weeks. At temperatures above 135° the yellow form becomes red if ground or compressed, and the yellow colour is restored when the stress is removed. Grinding or compression thus produce a metastable state, a fact confirmed by the differential heating curve of 3-hydroxy-9-phenylacridine against sodium chloride which indicated that an exothermic change occurs in the region of the red ⟶ yellow transformation.

It is unusual for grinding to make a crystalline solid amorphous, as it is for tautomerism to occur so readily in the solid state. These two phenomena probably are closely connected, and it is suggested that the yellow crystals of 3-hydroxy-9-phenylacridine contain lattices in the lactim form in which the hydroxyl groups are engaged in short hydrogen bonds with the nitrogen atoms of adjacent molecules. Tautomeric changes occur by proton transfer along these bonds. Grinding causes local heating, giving rise to disordered oxygen–nitrogen hydrogen bonds, and leading to local melting. The melt then contains a mixture of the tautomers which will recrystallise only very slowly since the regular system of hydrogen bonds, which provided the mechanism for the original tautomeric changes, has now been destroyed. The crystals are thus converted progressively into a glass. In Part I of this series it is shown that hydrogen bonds of the type postulated are particularly liable to become disordered.

Experimental

Ultraviolet spectra were measured with a Unicam S.P. 500 spectrophotometer. M.p.s were determined, and thermal behaviour between room temperature and 350° was examined, by means of a Kofler hot-stage microscope. The heating curve of 3-hydroxy-9-phenylacridine against sodium chloride was obtained in an apparatus described in the Thesis of one of us.[5]

[5] Cairns-Smith, Thesis, Edinburgh, 1956, p. 114.

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Thin films for spectroscopic examination were obtained by exposing in a vacuum of 0·4 mm. a silica plate (cooled by carbon dioxide–acetone) to the compound heated at 180—200° for 1—2 min.

3-Hydroxy-9-phenylacridine.—This compound was prepared by the recorded method [1] and chromatographed on alumina with chloroform as solvent and developer. A slow-moving upper red band and a fast-moving yellow band resulted. The latter on elution yielded a small amount of a substance, which is probably 1-hydroxy-9-phenylacridine since its ultraviolet spectrum resembled that of 4-hydroxyacridine.[2] The red band was removed by ethanol and yielded 3-hydroxy-9-phenylacridine, yellow needles (from benzene), m. p. 264° (lit.,[1] 264°) [*N*-methyl ether, m. p. 230° (lit., 231°)]. The hydroxy-compound (0·1 g.) in chloroform (3 ml.) was added in six portions to diazomethane in ether (prepared from 1 g. of *N*-nitrosomethylurea), and kept overnight at 0°. The solution was allowed to warm to room temperature and the solvent removed. The residue in chloroform was chromatographed on alumina and development with the same solvent gave a pale yellow band with a blue fluorescence, which yielded the *O-methyl ether*, a yellow green oil (0·4 g.); crystallised from absolute ethanol or light petroleum, this had m. p. 137—138° (Found: C, 84·3; H, 5·3; N, 4·9. $C_{20}H_{15}NO$ requires C, 84·2; H, 5·3; N, 4·9%).

Spectroscopic Measurements.—$\lambda_{max.}$ with log ε in parentheses and inflexions in italics were:

3-Hydroxy-9-phenylacridine: 258, *295*, 342, 356, 381, 402, *428* mμ in cyclohexane; 236, 259, 286, *322*, *338*, 352, 394, *410*, 483, *500* mμ (4·48, 4·89, 4·21, 3·39, 3·73, 3·99, 3·68, 3·58, 3·42, 3·35) in absolute ethanol; 236, *259*, 279, *355*, 365, 468 mμ (4·56, 4·42, 4·69, 4·05, 4·10, 3·98) in 20% aqueous ethanol.

3-Methoxy-9-phenylacridine: *239*, 260, *286*, *321*, 338, 352, 378, *393*, 398 mμ (4·52, 5·08, 3·70, 3·47, 3·76, 3·94, 3·84, 3·68, 3·71) in cyclohexane; 236, 258, *286*, 320, 335, 351, 380, *396* mμ (4·42, 5·07, 3·72, 3·47, 3·79, 4·02, 3·82, 3·67) in absolute ethanol.

10-Methyl-9-phenylacridine: 240, 294, 336, 351, *430*, 464, 490, *520* mμ in cyclohexane; 238, 288, 352, *363*, *450*, 478, 504 mμ (4·58, 4·69, 4·06, 4·03, 3·91, 4·07, 4·01) in absolute ethanol.

Thanks are expressed to the Department of Scientific and Industrial Research for the award of a Maintenance Grant (to A. G. C.-S.).

Department of Chemistry, University of Edinburgh. [*Received, May 2nd*, 1960.]

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234. *Syntheses of Thio-oxamides and Thioamides by Extensions of the Kindler Reaction.*

By Brian Milligan and J. M. Swan.

Further preparations of substituted thio-oxamides (II) from carbamoylmethyl thiolsulphates (I) are recorded and the reaction is extended to phenoxycarbonylmethyl and ethoxycarbonylmethyl thiolsulphates (III). Thio-oxamides are also obtained by heating chloroacetyl-, dichloroacetyl-, or trichloroacetyl-amines with sulphur and a primary or secondary amine, while benzyl chloride, benzylidene chloride, and benzotrichloride yield thiobenzoamides under the same conditions. Similar reaction of glyoxal, trichloroethylene, or tetrachloroethane with sulphur and an amine affords substituted dithio-oxamides.

Thiolsulphates (IV), prepared from halogenomethyl ketones, react with morpholine to give 4-acyl(thioformyl) derivatives (V) of morpholine.

In an earlier paper [1] it was shown that monothio-oxamides (II) are formed when carbamoylmethyl thiolsulphates (I) are heated with primary or secondary amines. Some further examples and various extensions and developments of this reaction are now reported.

(I) R·NH·CO·CH_2·S_2O_3Na RNH·CO·CS·NR′R″ (II)

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[1] Milligan and Swan, *J.*, 1959, 2969.

Schiff's bases or diaminomethylene compounds are believed to be intermediates in the Kindler reaction [2] and in these reactions of carbamoylmethyl thiolsulphates. Such compounds should also be formed by reaction of amines with dichloromethylene compounds, so that in the presence of sulphur these might also yield thioamides. When dichloroacetylamines were heated with sulphur and an amine monothio-oxamides were formed, often in very high yield. Thus *o*-dichloroacetamidobenzoic acid, cyclohexylamine, and one atomic proportion of sulphur gave N^{o}-*o*-carboxyphenyl-N^{s}-cyclohexyl(thio-oxamide) (II; R = $HO_2C{\cdot}C_6H_4$, R′ = C_6H_{11}, R″ = H), also obtained by heating the appropriate thiolsulphate (I; R = $HO_2C{\cdot}C_6H_4$) with cyclohexylamine. The corresponding N^{o}-*p*-carboxyphenyl-N^{s}-cyclohexyl(thio-oxamide) was similarly obtained. Dichloroacetanilide, sulphur, and cyclohexylamine, morpholine, or diethylamine gave thio-oxamides in yields greater than 90%. N^{s}-Cyclohexyl-N^{o}-phenyl(thio-oxamide) (II; R = Ph, R′ = C_6H_{11}, R″ = H), 4-(phenyl-α-thio-oxamoyl)morpholine * (II; R = Ph, R′R″ = $CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$), and N^{s}-diethyl-N^{o}-phenyl(thio-oxamide) (II; R = Ph, R′ = R″ = Et) were thus obtained. The reaction of dichloroacetamide with sulphur and cyclohexylamine gave N^{s}-cyclohexyl(thio-oxamide) (II; R = R′ = H, R″ = C_6H_{11}) in almost quantitative yield, but with morpholine the yield of 4-(α-thio-oxamoyl)morpholine was only 11%. This product was also obtained from morpholine and sodium carbamoylmethyl thiolsulphate (I; R = H).

Dichloroacetic acid, when heated with cyclohexylamine and sulphur, gave only *NN*′-dicyclohexylthiourea in low yield. Presumably decarboxylation here occurs to give dicyclohexylaminomethane, and the methylene group is then oxidised by sulphur to CS. The same thiourea was obtained on heating either methylene chloride or chloroform with sulphur and cyclohexylamine; methylene chloride, sulphur, and benzylamine gave the corresponding *NN*′-dibenzylthiourea but with morpholine the only product isolated was apparently 4-thioformylmorpholine. No crystalline product was obtained from reaction of carbon tetrachloride, sulphur, and amines.

The analogous chloromethyl and trichloromethyl compounds also yielded the same thioamides when heated with sulphur and an amine; the yields from the former were higher when two atomic proportions of sulphur were used. Thus chloroacetanilide, sulphur, and either cyclohexylamine or morpholine gave N^{s}-cyclohexyl-N^{o}-phenyl(thio-oxamide) and 4-(phenyl-α-thio-oxamoyl)morpholine, respectively; the same products were also obtained in fair yield from trichloroacetanilide. Benzyl chloride with two equivalents of sulphur in either cyclohexylamine or morpholine gave *N*-cyclohexyl(thiobenzamide) and thiobenzomorpholide, respectively. These same products were also obtained from *S*-benzylthiouronium chloride, from benzylidene chloride, and from benzotrichloride. The best yields (75—99%) in all these experiments were obtained, as expected, from benzylidene chloride, and this compound also gave rise to *N*-benzyl(thiobenzamide) on being heated with sulphur and benzylamine.

N-Cyclohexyl(thiobenzamide) and thiobenzomorpholide were also prepared by heating the appropriate amine with sulphur and benzaldehyde. In addition, thiobenzomorpholide was obtained on heating benzylideneaniline with morpholine and sulphur. When aqueous glyoxal was heated with sulphur and cyclohexylamine, the expected product, *NN*′-dicyclohexyl(dithio-oxamide) was formed. No crystalline product was obtained when either morpholine or aniline was used in place of cyclohexylamine. Better results were obtained by replacing the glyoxal with trichloroethylene or tetrachloroethane. These new syntheses of dithio-oxamides are somewhat analogous to earlier methods, in which either acetylene [3,4] or a vinyl ether or ester [5] is heated with sulphur and an amine. The synthesis of

* The nomenclature used is discussed in the previous paper.[1]

[2] King and McMillan, *J. Amer. Chem. Soc.*, 1948, **70**, 4143.
[3] Levesque, U.S.P., 2,525,075/1950; *Chem. Abs.*, 1951, **45**, 2499.
[4] Consonno and Cruto, *Gazzetta*, 1921, **51**, 181.
[5] Levesque, U.S.P., 2,531,283/1950; *Chem. Abs.*, 1951, **45**, 3412.

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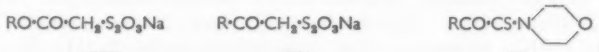
NN'-diphenyl(dithio-oxamide) by heating tetrabromoethane with aniline in alcoholic alkali, and then heating the unstable product with sulphur, has also been reported.[6]

In the reaction of thiolsulphates with amines,[1] only carbamoylmethyl thiolsulphates (I) yielded thio-oxamides when heated with amines, while other thiolsulphates were converted into disulphides. We have now found that sodium phenoxycarbonylmethyl thiolsulphate (III; R = Ph) and sodium ethoxycarbonylmethyl thiolsulphate (III; R = Et) react with cyclohexylamine and also with benzylamine to yield *NN'*-dicyclohexyl- and *NN'*-dibenzyl-(thio-oxamide), respectively. The phenoxy-compound also reacted with aniline to give the *NN'*-diphenyl compound. *NN'*-Dicyclohexyl(thio-oxamide) was also obtained when sodium anilinocarbamoylmethyl thiolsulphate (I; R = PhNH) was heated



(III) (IV) (V)

with cyclohexylamine. In these reactions, the first step may well be replacement of the phenoxy-, ethoxy-, or phenylhydrazino-group by amine, so that the subsequent reaction proceeds through a carbamoylmethyl thiolsulphate. However, a true variant of the thiolsulphate ⟶ thioamide reaction is the synthesis of 4-benzoyl(thioformyl)morpholine (V; R = Ph) from sodium phenacyl thiolsulphate (IV; R = Ph) and morpholine. 4-Acetyl(thioformyl)morpholine (V; R = Me) was prepared similarly from the crude thiolsulphate derived from bromoacetone.

Experimental

The light petroleum used had b. p. 55—70°. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory.

N°-p-*Carboxyphenyl*-N^{s}-*cyclohexyl*(*thio-oxamide*).—(i) *p*-Chloroacetamidobenzoic acid and sodium thiosulphate (1 equiv.) were heated under reflux in aqueous 2-methoxyethanol for 30 min. Excess of cyclohexylamine was added and boiling was continued for 5 min. The yellow precipitate was crystallized from ethanol. The *cyclohexylammonium salt* of *N°-p*-carboxyphenyl-*N^{s}*-cyclohexyl(thio-oxamide) separated as yellow needles, m. p. 228° (Found: C, 62·2; H, 7·7; N, 9·8; S, 7·8. $C_{21}H_{31}N_3O_3S$ requires C, 62·2; H, 7·7; N, 10·4; S, 7·9%). This salt was dissolved in chloroform and shaken with excess of 10% sodium hydroxide solution. Acidification of the aqueous phase gave N°-p-*carboxyphenyl*-N^{s}-*cyclohexyl*(*thio-oxamide*), yellow needles, m. p. 248° (from ethanol) (Found: C, 59·1; H, 6·0; N, 8·7; S, 10·4. $C_{15}H_{18}N_2O_3S$ requires C, 58·8; H, 5·9; N, 9·2; S, 10·5%).

(ii) Crude *p*-dichloroacetamidobenzoic acid (2·2 g., from 2·8 g. of the amine), sulphur (0·28 g.), and cyclohexylamine were heated under reflux for 5 min., and then ethanol was added. The yellow cyclohexylammonium salt of *N°-p*-carboxyphenyl-*N^{s}*-cyclohexyl(thio-oxamide) (2·34 g., 65% based on *p*-dichloroacetamidobenzoic acid) had m. p. 223° raised to 228° on crystallization from ethyl acetate. The m. p. was undepressed on admixture with a sample prepared by method (i).

N°-o-*Carboxyphenyl*-N^{s}-*cyclohexyl*(*thio-oxamide*).—(i) Anthranilic acid was converted *via* its *N*-chloroacetyl derivative into the corresponding Bunte salt (3 g.) which was heated under reflux with cyclohexylamine (10 ml.) for 5 min., and the mixture poured into a mixture of excess of dilute hydrochloric acid and ethyl acetate. The yellow *cyclohexylammonium salt* (0·25 g.) of *N°-o*-carboxyphenyl-*N^{s}*-cyclohexyl(thio-oxamide) was crystallized from ethanol. Yellow needles, m. p. 221°, were obtained (Found: C, 62·2; H, 7·6; N, 10·4; S, 8·0. $C_{21}H_{31}N_3O_3S$ requires C, 62·2; H, 7·7; N, 10·4; S, 7·9%). The ethyl acetate layer was extracted several times with 5% sodium hydroxide solution. These extracts slowly deposited yellow needles (1·06 g.), identified as the *sodium salt* of *N°-o*-carboxyphenyl-*N^{s}*-cyclohexyl(thio-oxamide) (Found: C, 52·8; H, 5·4; N, 8·4; S, 9·5. $C_{15}H_{17}N_2O_3SNa,H_2O$ requires C, 52·0; H, 5·5; N, 8·1; S, 9·3%). Acidification of the alkaline extracts gave N°-o-*carboxyphenyl*-N^{s}-*cyclohexyl*(*thio-oxamide*) (0·73 g.), yellow needles, m. p. 170° after crystallization from carbon tetrachloride–light petroleum. The Lassaigne test showed presence of halogen (Found: C, 54·1; H, 5·3; N, 8·2; S, 9·4. $C_{15}H_{18}N_2O_3S,\frac{1}{4}CCl_4$ requires C, 53·1; H, 5·3; N, 8·1; S, 9·3%).

[6] Ssabanejew and Prosin, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 233; 1902, **34**, 405.

(ii) *N*-Dichloroacetylanthranilic acid (1·0 g.), sulphur (0·13 g.), and cyclohexylamine (5 ml.) were heated under reflux for 5 min. Ethanol (30 ml.) was added to the cooled mixture; the yellow cyclohexylammonium salt of N^{o}-*o*-carboxyphenyl-N^{s}-cyclohexyl(thio-oxamide) (1·37 g., 84%) had m. p. 218°, undepressed on admixture with a sample prepared by method (i).

Reaction of Dichloroacetanilide with Sulphur and an Amine.—(i) Dichloroacetanilide (1·0 g.), sulphur (0·16 g.), and cyclohexylamine (5 ml.) were heated under reflux for 5 min. N^{s}-Cyclohexyl-N^{o}-phenyl(thio-oxamide),[1] m. p. 130°, was obtained in 93% yield.

(ii) *N*-Phenyl-α-thio-oxamoylmorpholine,[1] m. p. 166°, was obtained in 93% yield by reaction of dichloroacetanilide, sulphur (1 atomic proportion), and morpholine.

(iii) Reaction of dichloroacetanilide (1·0 g.), sulphur (0·16 g.), and diethylamine (5 ml.) in a sealed tube at 150° for 5 min. gave N^{s}-diethyl-N^{o}-phenyl(thio-oxamide) (94% yield), plates (from aqueous ethanol), m. p. 125° (Found: C, 61·2; H, 6·6; N, 11·5; S, 13·8. $C_{12}H_{16}N_2OS$ requires C, 61·0; H, 6·8; N, 11·9; S, 13·6%).

(iv) No thio-oxamide was obtained by reaction of dichloroacetanilide, sulphur, and aniline.

N^{s}-*Cyclohexyl(thio-oxamide)*.—Dichloroacetamide (1·28 g.), sulphur (0·32 g.), and cyclohexylamine (10 ml.) were heated under reflux for 5 min. N^{s}-Cyclohexyl(thio-oxamide) (1·85 g., 99%) crystallized from light petroleum as yellow laths, m. p. and mixed m. p.[1] 108°.

4-(α-*Thio-oxamoyl)morpholine.*—(i) Impure sodium carbamoylmethyl thiolsulphate (2·0 g.) and morpholine (10 ml.) were heated under reflux for 5 min. The product (0·5 g.) crystallized from chloroform–light petroleum as pale yellow prisms, m. p. 160° (Found: C, 41·7; H, 5·9; N, 15·4; S, 18·4. $C_6H_{10}N_2O_2S$ requires C, 41·4; H, 5·8; N, 16·1; S, 18·4%).

(ii) By heating a mixture of dichloroacetamide (1·28 g.), sulphur (0·32 g.), and morpholine, 4-(α-thio-oxamoyl)morpholine (0·19 g., 11%) was obtained.

Reaction of Dichloroacetic Acid, Cyclohexylamine, and Sulphur.—Dichloroacetic acid (12·9 g.), sulphur (3·2 g.), and cyclohexylamine (30 ml.) were heated under reflux for 10 min. *NN'*-Dicyclohexylthiourea [7] crystallized from benzene–light petroleum as plates (0·98 g.), m. p. and mixed m. p. 178° after further crystallization from ethanol. Treatment of the product with peracetic acid gave *NN'*-dicyclohexylurea, m. p. 238° (lit.,[8] 229—230°), undepressed on admixture with an authentic sample, m. p. 238°.

Reaction of Methylene Chloride, Sulphur, and an Amine.—(i) Methylene chloride (1·70 g.), sulphur (1·28 g.), and cyclohexylamine (15 ml.) were heated in a sealed tube at 150° for 10 min. The neutral product (3·05 g.) gave *NN'*-dicyclohexylthiourea (0·92 g., 19%) after crystallization from benzene–light petroleum. (ii) Reaction of methylene chloride (2·0 g.), sulphur (1·5 g.), and benzylamine at 150° for 30 min. gave a neutral product (4·97 g.) from which *NN'*-dibenzylthiourea (2·71 g., 45%), m. p. 145° (lit.,[9] 146°) was obtained by crystallization from ethanol.

(iii) Reaction of methylene chloride, sulphur, and morpholine at 150° for 30 min. gave a product which was chromatographed on alumina. Elution with benzene–light petroleum (1 : 1) afforded crystalline material (0·5 g.), m. p. 64° after two crystallizations from water [presumably 4-(thioformyl)morpholine (lit.,[10] m. p. 67·5—68·5°)].

Reaction of Chloroform, Sulphur, and Cyclohexylamine.—(i) Chloroform (2·38 g.), sulphur (1·28 g.), and cyclohexylamine (15 ml.) were heated in a sealed tube for 10 min. The neutral product gave *NN'*-dicyclohexylthiourea (0·52 g., 11%) after crystallization from methanol.

Reaction of Chloroacetanilide, Sulphur, and an Amine.—(i) Chloroacetanilide (2·0 g.), sulphur (0·76 g.), and cyclohexylamine (10 ml.) were heated under reflux for 5 min. The mixture was partitioned between ethyl acetate and water, and the organic phase washed with dilute acid, dried, and evaporated. The residue, N^{s}-cyclohexyl-N^{o}-phenyl(thio-oxamide) (2·60 g., 84%), after crystallization from ethanol had m. p. and mixed m. p.[1] 130°. Addition of hydrochloric acid to the aqueous phase gave *N*-cyclohexyl(phenylcarbamoylmethyl)ammonium chloride, plates, m. p. >200° (from water) (Found: C, 62·4; H, 7·9; N, 10·2. $C_{14}H_{21}ClN_2O$ requires C, 62·6; H, 7·9; N, 10·4%). Neither this salt nor the parent amine gave any thio-oxamide when heated with sulphur and cyclohexylamine.

Reaction of chloroacetanilide, sulphur (1 atomic proportion), and cyclohexylamine as above gave the thio-oxamide in 48% yield.

(ii) Reaction of chloroacetanilide with sulphur (2 atomic proportions) and excess of

[7] Zetzsche and Fredrich, *Ber.*, 1940, **73**, 1114.
[8] Skita and Rolfes, *Ber.*, 1920, **53**, 1248.
[9] Werner, *J.*, 1891, **59**, 396.
[10] King and McMillan, *J. Amer. Chem. Soc.*, 1947, **69**, 1207.

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morpholine as in (i) gave *N*-phenyl-α-thio-oxamoylmorpholine (57%), m. p. and mixed m. p. 166° after crystallization from methanol. When only 1 atomic proportion of sulphur was used the yield fell to 44%.

Reaction of Trichloroacetanilide, Sulphur, and an Amine.—(i) Reaction of trichloroacetanilide, sulphur (1 atomic proportion), and cyclohexylamine gave N^{s}-cyclohexyl-N^{o}-phenyl(thio-oxamide) in 55% yield.

(ii) *N*-Phenyl-α-thio-oxamoylmorpholine was obtained in 63% yield by reaction of trichloro-acetanilide, sulphur (1 atomic proportion) and excess of morpholine.

Reaction of Benzyl Compounds, Sulphur, and an Amine.—(i) Benzyl chloride, sulphur (2 atomic proportions), and cyclohexylamine were heated under reflux for 5 min. *N*-Cyclohexyl-(thiobenzamide), yellow prisms, m. p. 89° (from ethanol), was obtained in 73% yield.

(ii) Reaction of benzyl chloride, sulphur (2 atomic proportions), and morpholine gave a 20% yield of thiobenzomorpholide, prisms, m. p. 137° (from ethanol).

(iii) Reaction of *S*-benzylthiouronium chloride, sulphur (2 atomic proportions), and morpholine gave thiobenzomorpholide in 71% yield. With cyclohexylamine in place of morpholine the yield of *N*-cyclohexyl(thiobenzamide) was 77%.

Reaction of Benzylidene Chloride, Sulphur, and an Amine.—(i) Benzylidene chloride (2·0 g.), sulphur (0·40 g.), and cyclohexylamine (10 ml.) were heated under reflux for 10 min., giving *N*-cyclohexyl(thiobenzamide) (2·7 g., 99%; 70% after crystallization from light petroleum).

(ii) Benzylidene chloride, sulphur (1 atomic proportion), and morpholine were heated; the neutral product gave thiobenzomorpholide (from ethanol) (1·83 g., 75%).

(iii) Reaction of benzylidene chloride, sulphur (1 atomic proportion), and benzylamine gave *N*-benzyl(thiobenzamide), yellow needles (57%), m. p. 87° (lit.,[11] 86°) (from light petroleum).

Reaction of Benzotrichloride, Sulphur, and an Amine.—(i) Benzotrichloride (1·95 g.), sulphur (0·64 g., 2 atomic proportions), and cyclohexylamine (10 ml.) were heated under reflux for 10 min. The neutral product gave *N*-cyclohexyl(thiobenzamide) (1·34 g., 61%) after crystalliz-ation from light petroleum.

(ii) With morpholine, thiobenzomorpholide (47% after crystallization from water) was obtained.

Reaction of Benzaldehyde, Sulphur, and an Amine.—(i) Thiobenzomorpholide (73%) was obtained by heating benzaldehyde, sulphur (1 atomic proportion), and excess of morpholine under reflux for 5 min.

(ii) With cyclohexylamine in place of morpholine, cyclohexyl(thiobenzamide) was obtained in 41% yield.

Reaction of N-*Benzylideneaniline, Sulphur, and Morpholine.*—Thiobenzomorpholide (90%) was obtained by heating benzylideneaniline, sulphur (1 atomic proportion), and morpholine under reflux for 10 min.

NN′-*Dicyclohexyl(dithio-oxamide).*—(i) Glyoxal (50%; 5 g.) was diluted with water (20 ml.), and cyclohexylamine was added with cooling. Sulphur (2·5 g.) was stirred in, and the mixture was heated to the b. p., cooled, and then acidified. Crystallization of the precipitate from ethanol gave *NN′*-dicyclohexyl(dithio-oxamide) (4·9 g., 41%), m. p. 150° after crystallization from acetic acid (Levesque [3,5] records m. p. 156—158°; Naylor and Hook [12] m. p. 145—147°) (Found: C, 59·4; H, 8·3; N, 9·3. Calc. for $C_{14}H_{24}N_2S_2$: C, 59·1; H, 8·5; N, 9·9%). Oxidation with peracetic acid gave *NN′*-dicyclohexyloxamide, m. p. and mixed m. p. 273°.

(ii) Trichloroethylene (2·6 g.), sulphur (1·28 g.), and cyclohexylamine (15 ml.) were heated in a sealed tube at 160° for 30 min. *NN′*-Dicyclohexyl(dithio-oxamide) (4·18 g., 74%) crystal-lized from n-butanol as prisms, m. p. 148°.

(iii) A mixture of tetrachloroethane (3·2 g.), sulphur (1·3 g.) and cyclohexylamine (20 ml.) was heated under reflux for 30 min. *NN′*-Dicyclohexyl(dithio-oxamide) (1·8 g., 65%) had m. p. 148° after one crystallization from ethanol.

4,4′-Dithio-oxaloylbismorpholine.—Tetrachloroethane (3·2 g.), sulphur (1·3 g.), and morpholine were heated under reflux for 3 hr. The neutral product (2·9 g.) gave 4,4′-dithio-oxaloylbis-morpholine (0·44 g., 10%) as pale yellow prisms, m. p. 255° after crystallization from benzene.

Sodium Phenoxycarbonylmethyl Thiolsulphate.—A mixture of phenyl chloroacetate (15 g.) and sodium thiosulphate pentahydrate (22 g.) in 50% aqueous ethanol (300 ml.) was heated

[11] Levi, *Gazzetta*, 1929, **59**, 548.
[12] Naylor and Hook, U.S.P., 2,723,969/1955; *Chem. Abs.*, 1956, **50**, 4548.

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under reflux for 1 hr., and the solvent was then evaporated *in vacuo*. The residue was extracted with boiling ethanol (200 ml.) from which the *thiolsulphate* (11·3 g., 48%) crystallized as needles, m. p. 151° (decomp.) (Found: C, 34·2; H, 3·4; S, 22·3. $C_8H_7O_6S_2Na,\frac{1}{2}H_2O$ requires C, 34·4; H, 2·9; S, 23·0%). The *anilinium salt* crystallized from water as needles, m. p. 161° (Found: C, 49·9; H, 4·7; N, 4·3; S, 18·6. $C_{14}H_{15}NO_5S_2$ requires C, 49·3; H, 4·4; N, 4·1; S, 18·8%). Treatment of an aqueous solution of sodium phenoxycarbonylmethyl thiolsulphate with bromine water gave a precipitate of *di(phenoxycarbonylmethyl) disulphide*, m. p. 117° (from methanol) (Found: C, 57·8; H, 4·2; S, 19·1. $C_{16}H_{14}O_4S_2$ requires C, 57·5; H, 4·2; S, 19·2%).

Sodium Ethoxycarbonylmethyl Thiolsulphate.—Similar reaction of ethyl chloroacetate and sodium thiosulphate gave *sodium ethoxycarbonylmethyl thiolsulphate* (64%), as prisms, m. p. 155° (from ethanol) (Found: C, 21·4; H, 3·3; S, 28·4. $C_4H_7O_5S_2Na$ requires C, 21·6; H, 3·2; S, 28·9%).

NN'-Dicyclohexyl(thio-oxamide).—(i) Sodium phenoxycarbonylmethyl thiolsulphate (0·5 g.) and cyclohexylamine (5 ml.) were heated under reflux for 5 min., cooled, and dissolved in ethyl acetate (30 ml.). The solution was washed with dilute hydrochloric acid and water, dried, and evaporated. Crystallization of the residue from ethanol gave *NN'*-dicyclohexyl(thio-oxamide) (0·36 g., 73%) as yellow plates, m. p. and mixed m. p.[1] 165°.

(ii) Similar reaction of sodium ethoxycarbonylmethyl thiolsulphate (1·0 g.) with cyclohexylamine and crystallization of the product from ethanol gave *NN'*-dicyclohexyl(thio-oxamide) (0·31 g., 26%).

NN'-Dibenzyl(thio-oxamide).—(i) Sodium phenoxycarbonylmethyl thiolsulphate and benzylamine were heated at 150° for 5 min., and the product was isolated in the usual way. *NN'*-Dibenzyl(thio-oxamide) (45% yield) formed yellow needles, m. p. 118—119°, from ethanol (Found: C, 67·6; H, 5·7; S, 11·4. $C_{16}H_{16}N_2OS$ requires C, 67·6; H, 5·7; S, 11·3%).

(ii) Reaction of sodium ethoxycarbonylmethyl thiolsulphate and benzylamine gave *NN'*-dibenzyl(thio-oxamide) (52% yield).

No crystalline products could be obtained by reaction of either Bunte salt with morpholine, diethylamine, or dicyclohexylamine.

NN'-Diphenyl(thio-oxamide).—Reaction of sodium phenoxycarbonylmethyl thiolsulphate (0·5 g.) and boiling aniline (5 ml.) for 5 min. gave a crude product from which *NN'*-diphenyl(thio-oxamide) (0·11 g., 23%) was obtained as yellow needles, m. p. and mixed m. p.[1] 143° (from ethanol).

Thio-oxamides derived from N-Chloroacetyl-N'-phenylhydrazine.—*N*-Chloroacetyl-*N'*-phenylhydrazine [13] (30 g.) and sodium thiosulphate (1 equiv.) were heated in aqueous ethanol for 30 min. The solvent was evaporated and the residue extracted with boiling ethanol. The crude Bunte salt (17 g.) crystallized on cooling. It was very hygroscopic; the cyclohexylammonium and *S*-benzylthiouronium salts were also very soluble in water and could not be prepared in the usual way.

Reaction of the crude Bunte salt with cyclohexylamine under reflux for 10 min. gave *NN'*-dicyclohexyl(thio-oxamide), m. p. 165°, in about 10% yield.

Similar treatment of the crude Bunte salt with benzylamine gave *NN'*-dibenzyl(thio-oxamide), m. p. 118°, in low yield.

Sodium Phenacyl Thiolsulphate.—A mixture of phenacyl chloride (15·5 g.) in ethanol (50 ml.) and sodium thiosulphate pentahydrate (25 g.) in water (50 ml.) was heated to the b. p. and then evaporated to dryness under reduced pressure. The residue was extracted with boiling ethanol (150 ml.) from which the *Bunte salt* (18·0 g., 70%) crystallized as plates (Found: C, 37·7; H, 3·1; S, 25·0. $C_8H_7O_4S_2Na$ requires C, 37·8; H, 2·8; S, 25·2%). Baker and Barkenbus [14] describe the salt as a monohydrate. The infrared spectrum (KBr disc) showed strong absorption at 1673 cm.$^{-1}$ (CO group).

Oxidation of the Bunte salt with bromine water gave diphenacyl disulphide, m. p. 81° (lit.,[14] 81°). Infrared spectrum (KBr disc), 1665 cm.$^{-1}$ (CO group).

4-Benzoyl(thioformyl)morpholine.—A solution of sodium phenacyl thiolsulphate (1·0 g.) in morpholine (10 ml.) was heated at 100° for 15 min. *4-Benzoyl(thioformyl)morpholine* (0·64 g., 69%), isolated in the usual way, crystallized from ethanol as yellow plates, m. p. 117° (lit.,[16]

[13] Gattermann, Johnson, and Holze, *Ber.*, 1892, **25**, 1080.
[14] Baker and Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 262.
[15] Groth, *Arkiv Kemi, Min., Geol.*, 1924, **9**, 63.
[16] Barrett, *J.*, 1957, 2056.

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114°) (Found: C, 61·2; H, 5·5; N, 5·4; S, 13·4. Calc. for $C_{12}H_{13}NO_2S$: C, 61·3; H, 5·6; N, 6·0; S, 13·6%). Infrared spectrum (CCl_4 solution), 1673 cm.$^{-1}$ (CO group).

Oxidation with peracetic acid (40%) at 80° for 2 min. gave benzoic acid.

4-Acetyl(thioformyl)morpholine.—Bromoacetone (34 g.) in ethanol (100 ml.) and sodium thiosulphate pentahydrate (62 g.) in water (100 ml.) were heated at 65° for 10 min. Morpholine (50 ml.) was added to the hot solution. After 15 min. the mixture was acidified and extracted with ethyl acetate. Evaporation of the extract gave 4-acetyl(thioformyl)morpholine (8·0 g.), yellow needles, m. p. 125—126° after crystallization from ethanol (Found: C, 48·6; H, 6·3; N, 7·7; S, 18·8. $C_7H_{11}NO_2S$ requires C, 48·5; H, 6·4; N, 8·1; S, 18·5%).

We thank Mr. J. B. Caldwell for technical assistance, and Dr. E. Spinner for determination of the infrared spectra.

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[*Received, June 8th,* 1960.]

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235. *Iodine Complexes in Inert Solvents. Part IX.* The Reaction between Solid Sodium Hydroxide and Iodine dissolved in Inert Solvents.*

By P. A. D. de Maine and M. M. de Maine.

Quantitative data are given for the slow decoloration of iodine solutions in contact with solid sodium hydroxide. Carbon tetrachloride, cyclohexane, and n-heptane, which do not react with iodine or sodium hydroxide, were the solvents used. Empirical relations which describe the data are given.

The violet colour of iodine in contact with pellets of sodium hydroxide in inert solvents gradually disappears during several days. The pellets become pale brown within 2 hours of their addition to the iodine solutions, and they slowly swell to at least twice their initial volume. Absorption-spectra measurements showed that molecular iodine and solid sodium hydroxide do not themselves react with the inert solvents used. We now report a quantitative study of the reactions involved.

Experimental

Fisher Scientific Spectroanalysed Grade carbon tetrachloride, n-heptane, and cyclohexane, Fisher Scientific Certified Resublimed iodine, and Fisher Scientific Anhydrous diethyl ether were all used without further purification. They were shown not to contain detectable amounts of water. Certified Reagent Grade Electrolytic sodium hydroxide pellets, supplied by Fisher Scientific Company, and taken from four freshly opened bottles, were placed in a vacuum-desiccator (10^{-3} mm. Hg) for several hours, then stored in the pure solvent (previously saturated with dry nitrogen) of the system in which they were to be used. Sets of sample solutions were made by diluting measured portions of standard iodine-inert solvent solutions with the appropriate pure solvent to 50 or 100 ml. in volumetric flasks fitted with ground-glass stoppers.

Absorption spectra in the ultraviolet and visible region for each sample were measured against the appropriate pure inert solvent with a calibrated [1] Beckman DU Spectrophotometer. The samples were stored at set temperatures in the range −5 to 45°. The sodium hydroxide pellets were added to the temperature-equilibrated samples and the spectra were measured again before the fifth hour after addition of the pellets, and at stated times during the next week or two. In addition, the absorption spectra of a sample containing no sodium hydroxide, and that of solvent in contact with sodium hydroxide, were measured at the same times. Care was taken to minimize the loss of solution in filling and emptying the quartz spectrophotometer cells. Such losses could easily be kept under 1% of the original volume.

* Part VIII, de Maine and Peone, *J. Mol. Spectroscopy*, 1960, **4**, 262.

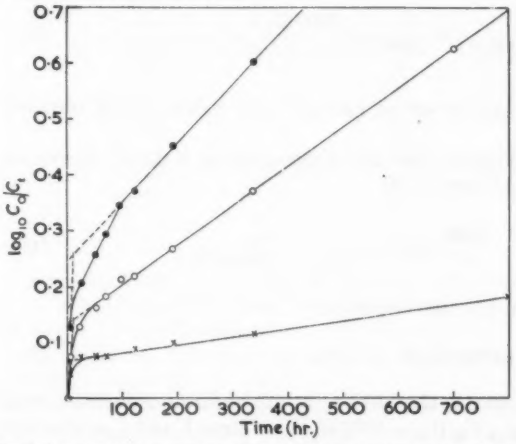
[1] de Maine, *J. Chem. Phys.*, 1957, **26**, 1192.

Results and Discussion

In separate experiments it was shown that the decoloration of iodine solutions in contact with solid sodium hydroxide is not due to any separate reaction between the iodine or sodium hydroxide and the solvent.

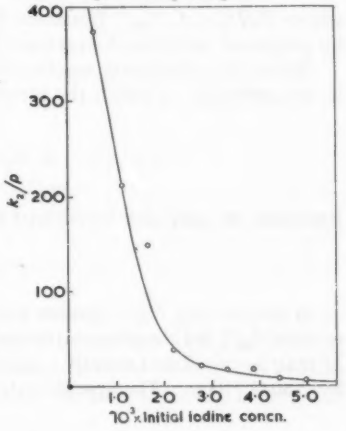
For the long-wavelength side of 3600 Å (the region where Beer's law is normally obeyed by iodine-inert solvent solutions) the ratio D_0/D_t (D_0 and D_t are optical densities measured at the same wavelength for a solution before addition of pellets and at t hours after the addition, respectively) will be independent of wavelength only if no new absorbing species pass into the solution during time t. In the present work D_0/D_t values at different times

Fig. 1. *Plots of $\log_{10}(C_0/C_t) \equiv (D_0/D_t)$ against time (hr.) for carbon tetrachloride–iodine solutions in contact with solid sodium hydroxide at 21°.*



The initial iodine concentration (mole/l.) and number of sodium hydroxide pellets in a 100 ml. flask of solution are as follows: ●, 3·319 × 10^{-3}, 3; ○, 2·766 × 10^{-3}, 2; ×, 4·425 × 10^{-3}, 2.

Fig. 2. *Plot of k_2/P against initial iodine concentration for iodine–carbon tetrachloride solutions in contact with solid sodium hydroxide at 21°. [k_2 is defined by equation (1) and P is the number of moles of iodine required to saturate unit absorbing surface of sodium hydroxide pellet.]*



are constant (maximum deviation less than 2%) for all wavelengths between 3600 and 7500 Å. For the spectral region to the short-wavelength side of 3600 Å where Beer's law is not normally obeyed because of the reversible reaction $2I_2 \rightleftharpoons I_4$, we have used published data [2-4] to confirm that no new species absorbing light between 2600 and 3600 Å passes into the solution.

For 53 of the 71 separate solutions studied, plots of $\log_{10} D_0/D_t$ against time, t, were linear after an interval of 8 hours. For the remaining solutions such plots yielded two intersecting straight lines. The time of these changes in slope corresponded to spontaneous fragmentation of one of the sodium hydroxide pellets in contact with the solution. Fig. 1 shows plots of both types.

If the decoloration mechanism is: I_2 in solution $\xrightarrow{k_1}$ I_2 adsorbed on to NaOH surface $\xrightarrow{k_2}$ I_2 transported into the solid sodium hydroxide, with $k_1 \ggg k_2$, two separate cases

[2] de Maine, *J. Chem. Phys.*, 1956, **24**, 1091; *Canad. J. Chem.*, 1957, **35**, 573.
[3] de Maine, de Maine, and McAlonie, *J. Mol. Spectroscopy*, 1960, **4**, 271.
[4] Keefer and Allen, *J. Chem. Phys.*, 1956, **25**, 1059.

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can be identified. During an initial period when adsorption predominates, decoloration can be described by the equation:

$$-10^{-3}V(\mathrm{d}C_t/\mathrm{d}t) = k_1(S - \Delta S_t)C_t \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_t is the iodine concentration (in moles/l.) in a solution of volume V c.c. standing over solid sodium hydroxide at time t. S and $(S - \Delta S_t)$ are the effective molecular surfaces at times zero and t respectively. If $M(=PS)$ is the number of moles of iodine required to saturate the surface, equation (1) can be written thus:

$$-10^{-3}V(\mathrm{d}C_t/\mathrm{d}t) = k_1C_t[M - 10^{-3}V(C_0 - C_t)]/P \quad . \quad . \quad . \quad . \quad (2)$$

where C_0 is the iodine concentration (moles/l.) before addition of the pellets. No assumptions are made as to the molecular depth of the adsorbed layers. Integration of equation (2) yields

$$k_1/P = \frac{V}{t(VC_0 - 1000M)} \ln \frac{1000MD_t}{1000MD_0 - VD_0(C_0 - C_t)} \quad . \quad . \quad . \quad (3)$$

where $D_t/D_0 = C_t/C_0$. Equation (3) can be solved for k_1/P with values for M obtained by graphical solution of equation (4).

When the adsorption reaction is complete, the rate of decoloration is described exactly by equation (5), of which the integrated form is (4):

$$\ln C_0/C_t = \ln D_0/D_t = \frac{1000}{V} k_2St + \ln \frac{C_0}{C_0 - 1000M/V} \quad . \quad . \quad . \quad (4)$$

Equation (4) may also be derived from the rate equation

$$-(V/1000)\,\mathrm{d}C_t/\mathrm{d}t = k_2SC_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A plot of $\log_{10} D_0/D_t$ against time (greater than 40 hr.) would be linear with slope equal to $1000Sk_2/2{\cdot}304V$ and one intercept $\log_{10}[C_0/(C_0 - 1000M/V)]$. Since V and C_0 are known, M may be calculated exactly; k_2/P can be obtained by dividing M into the slope multiplied by $2{\cdot}304V/1000$. The specific rate constants for the adsorption process (k_1/P) have been

TABLE 1. *Values for* k_2/P *in carbon tetrachloride at* 8° *in systems containing iodine and sodium hydroxide pellets.*

$1000C_0$ (mole/l.)	No. of NaOH pellets	k_2/P		$1000C_0$ (mole/l.)	No. of NaOH pellets	k_2/P	
1·241	1	16·6	Average 14·5	12·41	1	0·33	Average 0·29
1·241	2	12·9		12·41	2	0·22	
1·241	2	14·1		12·41	3	0·36	
				12·41	4	0·23	
3·102	2	1·03	Average 1·11	12·41	3	0·30	
3·102	2	1·12		12·41	1	0·27	
3·102	1	1·17					
8·686	2	0·30	Average 0·40				
8·686	2	0·50					

obtained by solving equation (3) with the values for M obtained by the method already given.

Data for the 53 samples which yielded straight-line plots for $\ln D_0/D_t$ against time after 8 hr. fit equation (5). The quantity k_2/P, which describes the second reaction, is independent of the molecular surface, S, of the solid hydroxide (Table 1) but is a function

of the initial molecular iodine concentration (Fig. 1). The quantity, k_1/P, which describes the irreversible adsorption of molecular iodine on to the surface of the solid material, is independent of the molecular surface, S, the initial iodine concentration, and the temperature (to a first approximation) (Table 2). Our calculations with data for carbon tetrachloride, n-heptane, and cyclohexane suggest that k_2/P and k_1/P are both independent of the nature of the solvent.

Analyses of the swollen pellets at the end of each experiment indicated that most of the absorbed material is actually present as molecular iodine. Thus the second reaction,

TABLE 2. *Values for* k_1/P, *from data for a time of* 5 *hr. and at the temperatures indicated.*

$1000C_0$ (mole/l.)	No. of pellets	Temp.	$10{,}000M$ (mole)	k_1/P	
1·111	3	2°	0·269	136·0	
1·090	1	2	0·112	114·5	Average
1·090	2	2	0·252	117·4	121·0
1·090	3	2	0·304	117·1	
1·106	2	21	0·493	110·7	
1·659	3	21	0·961	93·7	
2·212	1	21	0·518	94·0	Average
2·766	2	21	0·729	75·7	95·0
3·319	3	21	1·017	125·0	
3·872	1	21	0·430	77·4	
1·569	4	40	0·656	82·9	
1·678	2	40	0·292	98·1	Average
1·678	4	40	0·846	74·1	96·0
1·678	8	40	1·122	127·4	

which predominates after the eighth hour (see equation 5) may well describe the transportation of molecular iodine from the solution or the interface to inside the solid material. However, no mathematical relation between k_2/P and the initial iodine concentration could be found. Thus a complete examination in terms of known diffusion equations cannot be reported.

The irreversibility of the first step cannot be tested because M is approximately 2×10^{-5} mole per pellet while the concentration of the surrounding liquid is at least 10^{-3} mole/l. However, the consistency of the mathematical analysis clearly shows that a desorption process, if present, must be negligible in comparison with the adsorption process.

A search for alternative models to describe these data was unsuccessful.

One of us (P. de M.) is indebted to the Research Foundation of the State University of New York for a Summer Research Fellowship and for a grant towards equipment and supplies. He also thanks Professor W. C. Price for the use of experimental facilities at King's College, London, to carry out preliminary work on this problem in 1956.

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[*Received, June 29th,* 1960.]

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236. *Amino-sugars and Related Compounds. Part VIII.* Some Properties of 2-Deoxy-2-sulphoamino-D-glucose, Heparin, and Related Substances.*

By A. B. Foster, E. F. Martlew, M. Stacey, P. J. M. Taylor, and J. M. Webber.

A synthesis of the crystalline hydrated ammonium salt of 2-deoxy-2-sulphoamino-D-glucose (D-glucosamine *N*-sulphate) is described. The acid lability of its *N*-sulphate residue is compared with that of the similar group in heparin. The infrared spectra of heparin and a series of sulphated polysaccharides have been compared, but it has not been possible to detect an absorption characteristic of the *N*-sulphate group.

Recognition [1] of the presence of *N*-sulphated amino-sugar groups in heparin, the polysaccharide blood-anticoagulant present in mammalian circulatory tissue, has prompted attempts to synthesise model compounds. Meyer and Schwartz [2] obtained a mixture of *O*- and *N*-sulphated derivatives on treatment of 2-amino-2-deoxy-D-glucose [3] with a sulphur dioxide–trioxide mixture. Wolfrom, Gibbons, and Huggard,[4] using suitably blocked derivatives of 2-amino-2-deoxy-D-glucose with sulphur trioxide in pyridine, later prepared, *inter alia*, the *N*-sulphates of 2-amino-2-deoxy-D-glucose and methyl 2-amino-2-deoxy-α-D-glucopyranoside and isolated them as their hydrated sodium salts, of which that of the latter was crystalline. Only a brief description of some of the properties of these salts has appeared.[5]

We now report the crystalline hydrated ammonium salt of 2-deoxy-2-sulphoamino-D-glucose.

Treatment [6] of aqueous 2-amino-2-deoxy-D-glucose hydrochloride at pH 9—10 with the pyridine–sulphur trioxide complex,[7] although effecting *N*-sulphation, gave a mixture of products that were difficult to purify. When 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose [8] was treated with the pyridine–sulphur trioxide complex in a modification of Wolfrom, Gibbons, and Huggard's method,[5] *N*-sulphation occurred together with some de-*O*-acetylation and *O* ⟶ *N*-acetyl migration; this migration could not be prevented completely. The marked tendency of certain *O*-acetylated 2-amino-2-deoxy-D-glucose derivatives to undergo base-catalysed *O* ⟶ *N*-acetyl migration is well established.[9] De-*O*-acetylation of the crude 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-sulphoamino-β-D-glucose gave a mixture containing basic, neutral, and acidic components of which the last was 2-deoxy-2-sulphoamino-D-glucose subsequently isolated as the crystalline, hydrated ammonium salt. The salt appeared homogeneous on paper ionophoresis. 2-Deoxy-2-sulphoamino-D-glucose was obtained as an amorphous, hydrated sodium salt by Wolfrom *et al.*[4] from a crystalline, tetra-*O*-acetate precursor.

2-Deoxy-2-sulphoamino-D-glucose did not respond to the Morgan–Elson test [10] for

* Part VII, *J.*, 1960, 2587.

[1] For a review of heparin chemistry see Foster and Huggard, *Adv. Carbohydrate Chem.*, 1955, **10**, 335.
[2] Meyer and Schwartz, *Helv. Chim. Acta*, 1950, **33**, 1651; see also Wolfrom, Shen, and Summers, *J. Amer. Chem. Soc.*, 1953, **75**, 1519.
[3] Breuer, *Ber.*, 1898, **31**, 2193; Westphal and Holzmann, *ibid.*, 1942, **75**, 1274.
[4] Wolfrom, Gibbons, and Huggard, *J. Amer. Chem. Soc.*, 1957, **79**, 5043.
[5] Wolfrom, Gibbons, Huggard, and Neely, Abs. Papers, Amer. Chem. Soc. Meeting, Atlantic City, September, 1956, p. 21D.
[6] Warner and Coleman, *J. Org. Chem.*, 1958, **23**, 1133.
[7] Sisler and Audrieth, *Inorg. Synth.*, Vol. II, p. 173.
[8] Bergmann and Zervas, *Ber.*, 1931, **64**, 975; 1932, **65**, 1201.
[9] White, *J.*, 1938, 1498; Fodor and Ötvös, *Acta Chim. Acad. Sci. Hung.*, 1954, **5**, 205; *Chem. Ber.*, 1956, **89**, 701; van de Kamp and Micheel, *ibid.*, 1957, **90**, 2054.
[10] Morgan and Elson, *Biochem. J.*, 1934, **28**, 988; Aminoff, Morgan, and Watkins, *ibid.*, 1952, **51**, 379.

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reducing *N*-acetylated amino-sugars but gave a colour with $\lambda_{max.}$ 530 mμ (2-amino-2-deoxy-D-glucose gives a colour with $\lambda_{max.}$ 511 mμ) in the Elson–Morgan test [11] for reducing amino-sugars. The Elson–Morgan test was therefore deprived of convenience as a method for following the hydrolysis of the *N*-sulphate group. However, since 2-deoxy-2-sulphoamino-D-glucose gave a soluble salt with 4-amino-4′-chlorobiphenyl [12] and its presence did not interfere with the precipitation of sulphate by the reagent, it was possible to follow the hydrolysis of the *N*-sulphate group by using this base and Jones and Letham's spectrophotometric method.[13]

A 1% solution of ammonium 2-deoxy-2-sulphoamino-D-glucose in 0·1N-hydrochloric acid at 100° gave a hydrolysis constant k 6·24 × 10^{-2} min.$^{-1}$ for cleavage of the *N*-sulphate group. Wolfrom *et al.*[5] give k 5·6 × 10^{-2} min.$^{-1}$ for hydrolysis of the amorphous sodium salt carried out under similar conditions but followed by a different method.[14] Hydrolysis of a 1% solution of 2-deoxy-2-sulphoamino-D-glucose in 0·04N-hydrochloric acid at 100° gave k 1·84 × 10^{-2} min.$^{-1}$. The hydrolysis was essentially complete in 150 min. Various workers [15,16] have shown that, on treatment of heparin under similar conditions, hydrolysis of the *N*-sulphate group is essentially complete in 100—120 min. Thus, the acid-sensitivity of the polysaccharide *N*-sulphate moiety is not markedly influenced by its environment. Wolfrom and McNeely [16] found that a 2% solution of heparin (sodium or acid barium salt) in 11% acetic acid at 68° lost its anticoagulant activity in *ca.* 50 hr.; this treatment caused *ca.* 50% hydrolysis of the *N*-sulphate groups in the polysaccharide. After 50 hr. ammonium 2-deoxy-2-sulphoamino-D-glucose as a 1% solution in 11% acetic acid at 68° had undergone 31% hydrolysis.

Although hydrolysis of the *N*-sulphate group in heparin may be followed by 2,4-dinitrophenylation of the liberated amino-groups,[15] accurate determination of sulphate ion

Infrared spectral data ($\nu_{max.}$ *in 797—855 cm.*$^{-1}$ *region) for certain sulphated carbohydrates.*

Sulphated carbohydrate	S (%)	$\nu_{max.}$ [a] (cm.$^{-1}$)	Sulphated carbohydrate	S (%)	$\nu_{max.}$ [a] (cm.$^{-1}$)
Dextran sulphate	7·7	820	Chitin sulphate	11·45	810
Dextran sulphate	12·6	805	Chitosan sulphate	15·1	797
Dextran sulphate	18·6	810vb	Nigeran sulphate	14·7	805
1,6-Anhydro-β-D-glucose sulphate	16·1	812	Laminarin sulphate	14·9	803
Amylose sulphate	14·5	815	Chondroitin sulphate *A* [b]		852
Amylopectin sulphate	8·9	807	Chondroitin sulphate *B* [b]		855, 842
Glycogen sulphate	14·0	807	Chondroitin sulphate *C*		820 [c]
Cellulose sulphate	17·0	805b	Heparin	13·2	812
			De-*N*-sulphated heparin	8·05	817

[a] The spectra were determined for KCl or KBr discs. [b] Samples kindly provided by Prof. A. Dorfman. [c] Values taken from ref. 20.

in the early stages of hydrolysis is complicated by the presence of polysaccharide.[17] However, if acidic polysaccharide material in the hydrolysate is precipitated as the cetyltrimethylammonium salt,[18] the remaining sulphate ion may be determined by using 4-amino-4′-chlorobiphenyl. In this way a smooth release of sulphate ion was observed during the hydrolysis of heparin; a full account of these results is reserved for a future publication.

Treatment of heparin with 0·04N-hydrochloric acid at 95—100° for 2 hr. resulted in hydrolysis of all the *N*- and some of the *O*-sulphate groups,[15] to yield de-*N*-sulphated

[11] Elson and Morgan, *Biochem. J.*, 1933, **27**, 1824; see also Belcher, Nutten, and Sambrook, *Analyst*, 1954, **79**, 201; Rondle and Morgan, *Biochem. J.*, 1955, **61**, 586.
[12] Belcher, Nutten, and Stephen, *J.*, 1953, 1334.
[13] Jones and Letham, *Analyst*, 1956, **81**, 15.
[14] Professor M. L. Wolfrom, personal communication; Wolfrom, Gibbons, Huggard, and Neely, *J. Amer. Chem. Soc.*, in the press.
[15] Foster, Martlew, and Stacey, *Chem. and Ind.*, 1953, 899; Korn, *Biochem. J.*, 1959, **234**, 1321.
[16] Wolfrom and McNeely, *J. Amer. Chem. Soc.*, 1945, **67**, 748; Jorpes, Boström, and Mutt, *J. Biol. Chem.*, 1950, **183**, 607.
[17] Briscoe, Challenger, and Duckworth, *J.*, 1956, 1755.
[18] Bera, Foster, and Stacey, *J.*, 1955, 3788.

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heparin (ψ-heparin,[15] heparamine [19]). The S : N ratio of 1·33 for this polysaccharide corresponds to 2·66 *O*-sulphate groups per tetrasaccharide unit; normal heparin preparations contain two *N*- and three *O*-sulphate groups per tetrasaccharide unit. A comparison of the infrared spectra (KCl discs) of heparin and de-*N*-sulphated heparin revealed an overall similarity with only slight differences in the 925—975, 1100—1200, and 1490—1575 cm.$^{-1}$ regions and did not permit the identification of absorption characteristic of the *N*-sulphate group in the heparin spectrum. The location of absorption associated with N–H deformation in the *N*-sulphate group is unknown. Ammonium 2-deoxy-2-sulphoamino-D-glucose shows no absorption and *N*-isopropyltoluene-*p*-sulphonamide [17] only extremely weak absorption in the 1500—1600 cm.$^{-1}$ region where normal amides show strong absorption associated with N–H deformation. Weak, broad absorption at 1525 cm.$^{-1}$ shown by de-*N*-sulphated heparin, but not by heparin, may possibly be associated with the $-NH_3^+$ grouping; 2-amino-2-deoxy-D-glucose hydrochloride shows a strong absorption for this group at 1537 cm.$^{-1}$.

Axial sulphate groups (*e.g.*, as in galactopyranose 4-*O*-sulphate) in certain mono- and poly-saccharides show [20] absorption for C–O–S at *ca.* 850 cm.$^{-1}$ whereas hexopyranose 6-*O*-sulphates absorb at *ca.* 820 cm.$^{-1}$; the sulphated hydroxymethyl groups in the latter compounds are probably equatorial. However, from the absorptions recorded in the Table for a range of sulphated glucans, it seems unlikely that sulphated hydroxymethyl and equatorial secondary hydroxyl groups can be distinguished on the basis of absorption in the 800—820 cm.$^{-1}$ region. Absorptions within this region were shown by polysaccharides effectively containing solely sulphated hydroxymethyl groups (chondroitin sulphate *C*), sulphated equatorial secondary hydroxyl groups (dextran sulphates), or probably both (*e.g.*, amylose sulphate, nigeran sulphate, etc.). In addition to absorbing at 812—817 cm.$^{-1}$ heparin and de-*N*-sulphated heparin absorbed at 795 cm.$^{-1}$. It seems unlikely that the latter absorption is associated with the sulphate groups since, although it was also shown by amylose sulphate (792 cm.$^{-1}$) and amylopectin sulphate (787 cm.$^{-1}$), it was not shown by any other sulphated glucan examined.

Since heparin inhibits the growth of certain bacteria *e.g.*, *Micrococcus pyogenes*,[21] a series of heparin derivatives was prepared and tested for antibacterial activity. The free amino-group in de-*N*-sulphated heparin reacted readily with acid chlorides in water, acetone, or aqueous ethanol and in this way the following *N*-substituents were introduced: [22] benzoyl, benzyloxycarbonyl, *m*-trifluoromethylbenzoyl, nicotinoyl, isonicotinoyl, toluene-*p*-sulphonyl, *p*-acetamidobenzenesulphonyl, 2,4-dinitrophenyl, and di-*O*-phenylphosphoryl. Neither de-*N*-sulphated heparin nor any of the *N*-substitued derivatives antagonized the growth of selected strains of *Staphylococcus aureus*, *Escherichia coli*, and *Bacillus subtilis*. A parallel series of derivatives of isopropylamine was also prepared, some of which were hitherto unknown (see Experimental).

Since this work was completed,[23] a variety of *N*-substituted derivatives of de-*N*-sulphated heparin have been described [18,24] which paralleled heparin in clearing alimentary lipemia.[25]

Experimental

Ammonium 2-Deoxy-2-sulphoamino-D-glucose Hydrate.—A solution of 1,3,4,6-tetra-*O*-acetyl-β-D-glucose (10 g.; prepared according to Bergmann and Zervas's method [8]) in dry pyridine

[19] Velluz, Nomine, and Pierdet, *Compt. rend.*, 1958, **247**, 1521.
[20] Lloyd and Dodgson, *Nature*, 1959, **184**, 548, and references cited therein.
[21] Warren and Graham, *J. Bacteriol.*, 1950, **60**, 171; cf. Heilbrunn and Wilson, *Proc. Soc. Expt. Biol. Med.*, 1949, **70**, 179; Roth, *Arch. Biochem. Biophys.*, 1953, **44**, 265.
[22] A preliminary report of some of these results has been given by Foster, Martlew, and Stacey, Abs. Papers Amer. Chem. Soc. Meeting, New York, September 1954, p. 6D.
[23] Martlew, Ph.D. Thesis, University of Birmingham, 1954.
[24] Velluz, Plotka, and Nomine, *Compt. rend.*, 1958, **247**, 2203; Velluz, *Bull. Soc. Chim. biol.*, 1959, **41**, 415.
[25] Nikkila and Haahti, *Acta Chem. Scand.*, 1954, **8**, 363.

(170 ml.) was treated with pyridine–sulphur trioxide complex [7] (21 g.) at room temperature for 24 hr. The mixture was then added to a solution of sodium hydrogen carbonate (22 g.) in water (2·25 l.) at 0° and the resultant solution was freeze-dried. The residue was extracted thrice with methanol (total volume 300 ml.), and the combined extracts were evaporated yielding a glassy residue (12 g.). Examination of the residue by paper ionophoresis using the enclosed strip technique,[26] an acetate buffer (pH 5), and detection with alkaline silver nitrate [27] revealed a neutral component (probably arising by *O* ⟶ *N*-acetyl migration) and four acidic components with M_{GA} values (GA = D-gluconic acid) 1·00, 0·94, 0·875, and 0·815, the third predominating. The acidic components probably differ in the number of acetyl groups they contain since in the subsequent de-*O*-acetylation stage a single component of M_{GA} 1·00 was formed.

A small piece of clean sodium was added to a solution of the above product (11 g.) in dry methanol (300 ml.) at 0°, and the mixture was stored at 0° overnight. A precipitate (1·2 g.) separated which was collected and washed with cold methanol. Concentration of the mother-liquor (to *ca.* 60 ml.) gave a further yield (2·8 g.) of solid. Paper-ionophoretic examination (acetate buffer) of the two solid fractions and the remaining solution revealed, in each case, acidic (M_{GA} 1·00), neutral, and basic (trace) components in different proportions. The proportion of neutral component was greatest in the solution.

A portion (3 g.) of the combined solid products, dissolved in water (2 ml.), was absorbed on Deacidite FF (CO_3^{2-} form, 60 ml.). Elution with water (5 l.) removed the neutral and basic components and elution with 4% aqueous ammonium carbonate (700 ml.) removed most of the acidic compound. Ammonium carbonate was separated from the eluate by using Ultrasorb charcoal.[28] To improve the flow-rate, an Ultrasorb–Celite mixture, prepared according to Lindberg and Wickberg's general method [29] for charcoal–Celite mixtures, was used. The ammonium carbonate eluate was passed through a column (18 cm.) of Ultrasorb–Celite (180 ml.) and subsequent washing with water (650 ml.) removed most of the ammonium carbonate but no reducing sugar. Elution with a further amount (4 l.) of water removed the *N*-sulphate (1·17 g.). Recrystallization of the product from aqueous acetone gave *ammonium 2-deoxy-2-sulphoamino-D-glucose hydrate* as needles, m. p. 150—153° (decomp.) after darkening at *ca.* 130°, $[\alpha]_D^{20}$ +70·5° (2 min.) ⟶ +62° (equilibrium after *ca.* 3 hr.) (*c* 1·0 in water), $[M]_D$ +182° (Found: C, 24·4; H, 6·1; N, 9·75; S, 11·0. $C_6H_{16}N_2O_8S,H_2O$ requires C, 24·5; H, 6·1; N, 9·5; S, 10·9%). The infrared spectrum (Nujol mull) had an absorption at 1640 cm.$^{-1}$ indicative [30] of water of crystallization.

The *N*-sulphate appeared homogeneous on paper ionophoresis (acetate buffer) and detection with alkaline silver nitrate [27] and aniline hydrogen phthalate; [31] it did not react with ninhydrin.

Under the conditions recorded by Belcher, Nutten, and Sambrook [11] for the Elson–Morgan test, 2-deoxy-2-sulphoamino-D-glucose gave a colour with $\lambda_{max.}$ 530 mμ. Under the conditions given by Aminoff, Morgan, and Watkins [19] for the Morgan–Elson test, 2-deoxy-2-sulphoamino-D-glucose gave a negative result.

Acidic Hydrolysis of 2-Deoxy-2-sulphoamino-D-glucose.—Aliquot parts (0·1 ml., measured by a micro-syringe) of 1% solutions of ammonium 2-deoxy-2-sulphoamino-D-glucose hydrate in (*a*) 0·04N- and 0·1N-hydrochloric acid and in (*b*) 11% acetic acid sealed in ampoules were severally maintained at (*a*) 100° and (*b*) 68°. At intervals, ampoules were cooled and opened and the contents diluted so that the concentration of sulphate ion was within the range 60—200 μg./ml. The sulphate ion was then determined by Jones and Letham's method.[13]

Derivatives of Heparin.—The sodium heparinate used for the preparation of heparin derivatives was a commercial sample (Lederle Laboratories), $[\alpha]_D$ +46° (*c* 1·0 in H_2O) after drying at 110° for 3 hr. over phosphoric oxide, anticoagulant activity 80 I.U. per mg. [Found: N, 2·3; S, 13·2%; S : N ratio, 2·51. Calc. for $(C_{24}H_{31}N_2Na_7O_{35}S_5)_n$: N, 2·3; S, 13·0%; S : N ratio, 2·5]. Because of the extremely hygroscopic nature of the dried polysaccharide it was more convenient to analyze the polysaccharide in its normal, hydrated state and then correct the values for

[26] Foster, *Chem. and Ind.*, 1952, 1050.
[27] Trevelyan, Proctor, and Harrison, *Nature*, 1950, **166**, 444.
[28] Manufactured by British Carbo Norit Union Ltd., West Thurrock, Essex.
[29] Lindberg and Wickberg, *Acta Chem. Scand.*, 1954, **8**, 569.
[30] Barker, Bourne, and Whiffen, in "Methods of Biochemical Analysis," Interscience Publ. Inc., New York, 1956, Vol. III, p. 224.
[31] Partridge, *Nature*, 1949, **164**, 443.

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moisture content. The above analyses have been corrected for a 15% moisture content. The S : N ratio is independent of moisture content. A sample of a similar heparin preparation was dialysed against running water for 3 days and then isolated by freeze-drying; its infrared spectrum (KCl disc) showed the following absorptions (cm.$^{-1}$): 3460sb, 2980m, 2365w, 1637s, 1440s, 1230sb, 1155m, 1117m, 1030sb, 940msh, 885m, 817msh, 792m.

A 1% solution of sodium heparinate in 0·04N-hydrochloric acid was kept at 95—100° for 2 hr., then cooled, neutralized with sodium hydrogen carbonate, and dialysed against running water for several days. The dialysate was freeze-dried to yield the sodium salt of de-*N*-sulphated heparin having $[\alpha]_D$ +57° (*c* 1·0 in H_2O) after drying [Found: N, 2·65; S, 8·05%; S : N ratio, 1·33. Calc. for $(C_{24}H_{35}N_2Na_2O_{29}S_3)_n$: N, 2·85; S, 9·8%; S : N ratio 1·5. Calc. for $(C_{24}H_{36}N_2Na_2O_{26}S_2)_n$: N, 3·2; S, 7·3%; S : N ratio, 1·0]. The infrared spectrum (KCl disc) showed the following absorptions (cm.$^{-1}$): 3420sb, 2980m, 2370w, 1630s, 1527 wsh, 1430s, 1240sb, 1150m, 1030sb, 940m, 890m, 814m, 795m.

Biological Activity of Heparin Derivatives.—Serial dilutions of the *N*-substituted derivatives of de-*N*-sulphated heparin were prepared in nutrient broth (papain digest of beef) with a highest concentration of 1 mg./ml. Different tubes were inoculated with 24 hr. suspensions of *Staph. aureus* 663, *E. coli* 741, and *B. subtilis* 750 and incubated at 37°. After 24 hr., visual estimation of growth, as compared with controls, showed the absence of inhibitory activity.

Isopropylamine Derivatives.—Isopropylamine (7·5 g.) was added dropwise to a solution of acid chloride (7—10 g.) in carbon tetrachloride or benzene (100 ml.) with shaking and cooling. Isopropylamine hydrochloride was removed and the filtrate was washed successively with dilute hydrochloric acid, water, and aqueous sodium carbonate. Concentration of the dried ($MgSO_4$) solution gave the amide. The following derivatives were thus obtained: *benzyl* N-*isopropylcarbamate* (76%), m. p. 51—52°, b. p. 120° (bath)/0·05 mm. (Found: C, 68·1; H, 7·6; N, 7·0. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8; N, 7·25%); N-*isopropyl*-m-*trifluoromethylbenzamide* m. p. 88° (from aqueous ethanol) (Found: C, 57·7; H, 5·3; F, 24·2. $C_{11}H_{12}F_3NO$ requires C, 57·2; H, 5·2; F, 24·7%); p-*acetamido*-N-*isopropylbenzenesulphonamide* (81%), m. p. 163° (Found: C, 51·6; H, 6·4; N, 11·1; S, 12·5. $C_{11}H_{16}N_2O_3S$ requires C, 51·6; H, 6·25; N, 10·9; S, 12·5%); *diphenyl* N-*isopropylphosphoramidate* (91%), m. p. 73° (Found: C, 62·3; H, 6·5; N, 4·7; P, 10·5. $C_{15}H_{18}NO_3P$ requires C, 61·9; H, 6·2; N, 4·8; P, 10·7%); *phenyl* NN′-*di-isopropylphosphorodiamidate* (61%), m. p. 58—60° (Found: C, 56·2; H, 8·0; N, 10·9; P, 11·6. $C_{12}H_{21}N_2O_2P$ requires C, 56·3; H, 8·2; N, 10·9; P, 12·1%); NN′N″-*tri-isopropylphosphorotriamide* (77%), m. p. 124·5—125° (Found: C, 48·4; H, 10·7; N, 18·6; P, 13·95. $C_9H_{24}N_3OP$ requires C, 48·8; H, 10·9; N, 19·0; P, 14·0%).

m-Trifluoromethylbenzoyl chloride, prepared as was the *para*-isomer,[32] was an oil.

The authors thank Messrs. Glaxo Ltd. for determination of the antibacterial activities, the Evans Biological Institute for gifts of heparin, Dr. C. R. Ricketts for gifts of the sulphated glucans, and Dr. K. J. Morgan for discussion of the infrared spectra. One of them (J. M. W.) acknowledges an I.C.I. Fellowship, and others (E. F. M. and P. J. M. T.) thank D.S.I.R. for research studentships.

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[*Received, June 29th,* 1960.]

[32] Burger and Hornbaker, *J. Org. Chem.*, 1953, **18**, 192.

237. *Studies in the Light Absorption of Dyes. Part III.*[1] *Absorption Spectra of Dyes in Solution and Adsorbed in Solid Films.*

By C. H. Giles, S. M. K. Rahman, and (in part) D. Smith.

The absorption spectra have been examined of a large number of dyes of various chemical classes, including " reactive " dyes, in aqueous and non-aqueous solution, and adsorbed in solid transparent films. Almost all dyes have two absorption (x and y) wavebands. The shorter (y) waveband increases in height relative to the longer (x) with increase in concentration, in nearly all cases. This is attributed to aggregation. There is also a shift of both peaks with change in solvent (" solvatochromic " effect). The statistical significance of the method is examined.

The relation between colour and constitution of dyes has been discussed by many authors,[2] but the identification of absorption bands with aggregated states has received little attention except in the case of the cyanine photographic sensitising dyes (see, *e.g.*, ref. 2*c*) and certain basic dyes,[3-5] especially Methylene Blue.[3]

Lewis and Calvin [4] suggested that the absorption spectrum of a substance with a planar or almost planar molecule should consist of bands corresponding severally to electronic oscillations along the three perpendicular axes of the molecule. The shorter the axis, the shorter the wavelength of its band. This suggestion was confirmed experimentally by Lewis and Bigeleisen [5] for several basic dyes. When the molecules aggregate they may pack face-to-face, and the axis normal to the faces, originally one of the shorter ones, is lengthened. Thus the aggregate should have an intensified *short* waveband. This is in fact found with a number of dyes which display two well-defined absorption bands,[3,4] *e.g.*, Methylene Blue (C.I. 52,015).

The cyanine dyes, which have been studied exhaustively, show, *e.g.*, the main absorption band of the monomeric form of the dye (often termed the " M-band ") in dilute aqueous solution or in non-aggregating solvents, *e.g.*, pyridine. A shoulder on the short-wave side of this band becomes more pronounced (" D-band ") as the concentration in water increases, and is usually attributed to a dimeric form. This band shifts gradually to shorter wavelengths with increase in concentration, owing to the formation of larger aggregates (and is then called the " H-band "). In presence of certain electrolytes an entirely new, sharp, band appears on the long-wave side of the M-band. This is known as the " J-band," and is attributed to chain-like aggregates in which the planar dye molecules are packed face-to-face with a layer of water molecules between each pair of dye molecules.

Lewis and Bigeleisen also detected second-order x-bands in absorption spectra of some dyes.[6] The wavelengths of these bands are about half those of the first-order bands, whereas the y-bands are usually at only slightly shorter wavelengths than the x-bands.

Little is known about the occurrence of these bands in the spectra of other dyes, except vat dyes in non-aqueous solvents; [7] and apart from the investigations upon cyanine dyes

[1] The paper by Campbell, Cathcart, Giles, and Rahman, *Trans. Faraday Soc.*, 1959, **55**, 1631, is considered to be Part II of this series.

[2] See, *e.g.*, (*a*) Maccoll, *Quart. Rev.*, 1947, **1**, 16; (*b*) Lewis, *J. Amer. Chem. Soc.*, 1945, **67**, 770; (*c*) Dickinson, *Phot. J.*, 1950, **90***B*, 142; *J. Phot. Soc.*, 1954, **2**, 50 (cyanine sensitising dyes); (*d*) Knott, *J.*, 1951, 1024; (*e*) Brooker, *J. Amer. Chem. Soc.*, 1951, **73**, 5332, 5350, 5356 (merocyanine dyes); (*f*) Brooker, White, Heseltine, Keyes, Dent, and Van Lare, *J. Phot. Sci.*, 1953, **1**, 173 (cyanine sensitising dyes); (*g*) Brode, Gould, and Wyman, *J. Amer. Chem. Soc.*, 1953, **75**, 1856 (azo-dyes, effect of solvents); (*h*) Peters and Sumner, *J. Soc. Dyers and Colourists*, 1956, **72**, 77 (anthraquinone dyes); (*i*) Carroll and West, " Fundamental Mechanisms of Photographic Sensitivity," Butterworths, London, 1951.

[3] Rabinowitch and Epstein, *J. Amer. Chem. Soc.*, 1941, **63**, 69; Lemin and Vickerstaff, *Trans. Faraday Soc.*, 1947, **43**, 491; Förster and König, *Z. Electrochem.*, 1957, **61**, 344; Campbell and Giles, *J. Soc. Dyers and Colourists*, 1958, **74**, 164.

[4] Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273.

[5] Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2102.

[6] Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2107.

[7] Moran and Stonehill, *J.*, 1957, 765, 779.

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TABLE 1. *Absorption data (x- and y-bands) for dyes in various media.*

Dye	Medium *	$\lambda_{max.}$ † y	$\lambda_{max.}$ † x	O.D. at $\lambda_{max.}$ (x) in 1 cm. cell	O.D. ratio y : x
	Anthraquinone dyes				
C.I. 62,085	1 : 1 H_2O–pyridine	5800	6250	0·602 [1]	0·92
	,, ,,	5800	6250	1·300	0·93
	,, ,,	5800	6250	1·460	0·94
	0·2M-Phenol	5800	6200	0·264	0·95
	,,	5800	6200	1·276	0·97
	H_2O	5800	6100	0·349 [2]	0·96
	,,	5800	6100	0·918	0·99
	,,	5800	6100	1·259	0·98
	Gelatin	5850	6250	0·125	0·92
	,,	5850	6250	0·270	0·96
	,,	5850	6250	0·804	1·02
	,,	5850	6250	1·080	1·05
C.I. 63,010	1 : 1 H_2O–pyridine	6000	6450	0·167	0·91
	,,	6000	6450	0·749 [3]	0·91
	Gelatin	(6100)	6500	0·108	0·93
	,,	(6100)	6500	0·250	0·94
	,,	(6100)	6450	0·355	0·95
	Monoazo dye, unsulphonated				
p-Dodecylaniline ⟶ 2-naphthol	Ethylmethyl-cellulose film	4200	4800	0·315	0·80
	Collodion film	4200	5000	0·920	0·65

(This dye is more highly aggregated in the hydrophilic than in the hydrophobic film.)

	Monazo-dyes, sulphonated				
Aniline ⟶ naphthionic acid	Pyridine	4400	4750	0·344 [4]	0·89
	MeOH	(4200)	4600	0·447 [5]	0·76
	H_2O	(4200)	4600	0·459 [6]	0·80
	,,	(4200)	4600	1·760	0·85
	,,	(4200)	4600	2·46	0·91
	M-NaCl	(4200)	4600	0·557	0·83
C.I. 16,255	MeOH	5100	(5300?)	1·150 [7]	1·11
	Gelatin (dyed in 0·5M-phenol)	5150	(5450)	1·000	1·28
	Gelatin (dyed in 0·25M-phenol)	5150	(5450)	2·910	1·29
	Gelatin	5150	(5450)	1·580	1·30
C.I. 18,050	H_2O	5050	5300	0·447 [8]	1·01
	,,	5050	5300	0·720	1·01
	,,	5050	5300	0·955	1·01
	,,	5050	5300	3·048	1·03
p-Dodecylaniline ⟶ *N*-acetyl-H-acid	H_2O	5150	5450	0·110 [28]	1·00
	,,	5150	5450	0·902	1·02
	,,	5150	5450	3·480 [30]	1·09¶
	Gelatin (dyed in 2M-phenol)	5200	5550	0·825	1·13
	Gelatin	5200	5550	0·081	1·10
	,,	5200	5550	0·435	1·16
	,,	5200	5550	0·880	1·23
	Monazo-dyes,sulphonated				
Aniline ⟶ R-acid	MeOH	4850	5050	0·305 [9]	1·03
	H_2O	4950	5050	0·580 [10]	1·04
	Gelatin	4950	(5150)	0·280	1·09
p-Dodecylaniline ⟶ R-acid	MeOH	4950	(5200)	0·200 [11]	1·12
	H_2O	5000	(5270)	0·280 [12]	1·10
	0·2M-phenol	4950	(5350)	0·190	1·14
	Gelatin	5050	(5350)	0·190	1·08
Dye IV §	H_2O	4100	(4400)	0·349 [13]	1·27
	,,	4000	(4400)	0·569	1·50
	Gelatin	4000	(4400)	0·086	1·38
Dye V §	H_2O	4050	(4400)	0·182	1·59
	,,	4050	(4400)	0·445	1·66
	Gelatin	4000	(4400)	0·185	1·75
Dye VI §	1 : 1 H_2O-pyridine	4800	(5300)	0·137	2·31
	H_2O	4800	(5300)	0·165	2·54
	Gelatin	4800	(5300)	0·147	2·56
Dye VII §	1 : 1 H_2O–pyridine	4900	(5300)	0·078 [14]	1·46
	Gelatin (+CTAB)	4800	(5300)	0·135	1·74
	H_2O	5000	(5300)	0·211 [15]	1·13
	Gelatin	4950	(5300)	0·168	1·42

(CTAB = cetyltrimethylammonium bromide; this cationic agent increases the association of the dye.)

	Bis- and tris-azo-dyes, sulphonated				
C.I. 23,910	0·2M-Phenol	5050	(5450)	0·162	1·23
	,,	5050	(5450)	0·730	1·49
	H_2O	5100	(5450)	0·165	1·34
	,,	5100	(5450)	0·780	1·60
C.I. 24,140	Pyridine	(5500)	5930	0·760 [16]	0·77
	MeOH	(5500)	5750	0·680 [17]	0·93
	Cellulose	5850	(6350)	0·690	1·27
C.I. 24,410 (Sky Blue FF)	1 : 1 H_2O–pyridine	(5900)	6300	0·160 [18]	0·83
	,,	(5900)	6300	0·771	0·83
	,,	(5900)	6300	1·520	0·84
	H_2O	(5900)	6200	0·061 [20]	0·87
	,,	(5900)	6200	0·084 [21]	0·89
	,,	(5900)	6200	0·346 [22]	0·89
	,,	(5900)	6200	1·250 [23]	0·89
	,,	(5900)	6200	1·490 [24]	0·94
	Cellulose	6100	6600	0·294 [25]	0·80
	,,	6100	6600	0·820	0·80
	,,	6100	6550	1·900	0·89
	Gelatin	(6100)	6250	0·165	0·96
	,,	(6100)	6250	0·552	0·98
	,,	(6100)	6250	0·956	0·98
	,,	(6100)	6250	1·800	1·04
Copper complex of C.I. 24,410	1 : 1 H_2O–pyridine	(6200)	(6600)	0·139	1·01
	,,	(6200)	(6600)	0·561	1·03
	,,	(6200)	(6600)	1·480	1·07
	Bis- and tris-azo-dyes, sulphonated				
	H_2O	(6150)	(6750)	0·133 [12]	1·40
	,,	(6250)	(6750)	0·424	1·35
	,,	(6250)	(6750)	1·260	1·36
	Reactive dyes for cellulose				
Cibacron Rubine R	H_2O	(4950)	5250	0·125 [25]	0·76
	,,	(4950)	5250	0·498	0·80
	,,	(4950)	5250	1·250	0·80

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	2M-phenol)				
	Gelatin	5200	5550	0·081	1·10
	,,	5200	5550	0·435	1·16
	,,	5200	5550	0·880	1·23
	Bis- and tris-azo-dyes, sulphonated				
	H_2O	(6150)	(6750)	0·133 [19]	1·40
	,,	(6250)	(6750)	0·424	1·35
	,,	(6250)	(6750)	1·260	1·36
	Cellulose	(6300)	(6650)	0·137 [36]	0·99
	,,	(6300)	(6650)	0·555	1·00
	,,	(6300)	(6650)	0·678	1·06
C.I. Direct Blue 66 (trisazo)	1 : 1 H_2O–pyridine	(5900?)	6400	0·118 [20]	0·67
	,,	(5900?)	6500	0·540	0·70
	,,	(5900?)	6500	1·49	0·70
	H_2O	(6000?)	(6300?)	0·102 [21]	0·90
	,,	(6000?)	(6300?)	0·554	0·91
	,,	(6000?)	(6300?)	1·680	0·96
	Cellulose	(5900?)	6400	0·218 [37]	0·69
	,,	(5900?)	6400	1·100	0·71
	,,	(5900?)	6400	2·230	0·79
	Gelatin	(5900?)	6350	0·222	0·80
	,,	(5900?)	6350	0·335	0·82
	,,	(5900?)	6350	1·000	0·86
Polar Yellow R	0·2M-Phenol	(4100)	(4400)	0·150	0·97
	,,	(4100)	(4400)	1·370	1·06
	Cellulose	(4100)	(4400)	0·420	0·98
	H_2O	(4100)	(4400) 0·1400 l.$^{-1}$	0·245	1·02
	,,	(4100)	(4400) 0·7200 l.$^{-1}$	1·150	1·02
	Gelatin	(4100)	(4400)	0·323	1·03
	,,	(4100)	(4400)	1·370	1·06
	Metal-unsulphonated ligand (1 : 2) dyes				
Irganol Blue BS	H_2O	(5750)	6200	0·091 [22]	0·85
	,,	(5750)	6200	0·364	0·86
	,,	(5750)	6200	1·400	0·88
	Pyridine	(5850)	6250	0·116 [23]	0·85
	,,	(5850)	6250	0·414	0·90
	,,	(5850)	6250	1·060	0·91
	Gelatin	(5850)	6250	0·104	0·93
	,,	(5850)	6250	0·310	0·94
	,,	(5850)	6250	1·430	0·96
Irgalan Orange RL (C.I. Acid Orange 86)	H_2O	4800	(5300?)	0·062 [38]	1·65
	,,	4800	(5300?)	0·283 [39]	1·73
	,,	4800	(5300?)	1·105 [40]	1·70
	Gelatin	4900	(5400?)	0·475	1·54
	,,	4900	(5400?)	0·980	1·54
	,,	4900	(5400?)	1·720	1·56
	Pyridine	5000	(5400?)	0·590 [24]	1·40
	,,	5000	(5400?)	1·370	1·43
Copper complex of C.I. 24,410	1 : 1 H_2O–pyridine	(6200)	(6600)	0·139	1·01
	,,	(6200)	(6600)	0·561	1·03
	,,	(6200)	(6600)	1·480	1·07
	Reactive dyes for cellulose				
Cibacron Rubine R	H_2O	(4950)	5250	0·125 [25]	0·76
	,,	(4950)	5250	0·498	0·80
	,,	(4950)	5250	0·995	0·83
	,,	(4950)	5250	1·990	0·86
	Cellulose (after alkali-treatment)	(5050?)	(5500?)	0·111	0·91
	,, ,,	(5050?)	(5500?)	0·545	1·01
	,, ,,	(5050?)	(5500?)	1·300	1·08
Cibacron Scarlet 2G	H_2O	5000	(5290?)	0·158	1·10
	,,	5000	(5200?)	0·586	1·14
	,,	5000	(5200?)	1·820	1·14
	2% Na_2CO_3 (cooled after boiling 30 min.)	4950	(5200?)	0·204	1·23
	,, ,,	4950	(5250?)	0·541	1·28
	Cellulose (after alkali-treatment)	5100	(5350)	0·068	1·02
	,, ,,	5100	(5350)	0·73	1·12
	,, ,,	5100	(5350?)	1·46	1·12
Procion Brilliant Blue H7G (phthalocyanine derivative)	H_2O	6200	6600	0·074 [41]	0·43
	,,	6200	6600	0·382 [42]	0·68
	,,	6200	6600	1·340 [43]	0·81
	Cellulose	6250	6630	0·162	0·57
	,,	6250	6630	0·494	0·65
	,,	6250	6630	1·460	0·66
	2% Na_2CO_3 (after boiling 30 min.)	6300	6630	0·106	0·68
	,, ,,	6300	6650	0·410	0·71
	Pyridine	6070	6700	0·162 [26]	0·25
	,,	6070	6700	0·632	0·28
	,,	6050	6650	1·300	0·34
	Triphenylmethane dye				
C.I. 42,000 (Malachite Green)	H_2O	(5750)	6200	0·098 [27]	0·47
	,,	(5750)	6200	0·368	0·46
	,,	(5750)	6200	2·460	0·53
	Cellulose	(5750)	6300	0·790	0·45
	Cellulose acetate	(5750)	6300	0·363	0·33
	Gelatin	(5750)	6300	0·361	0·39
	,,	(5750)	6200	1·080	0·39

* Solvent ratios are v/v.

† Wavelengths are given in parentheses where the peak is flat or in the form of a shoulder; a query indicates a very indefinite peak.

Concns. can be determined from the following data for optical densities. For concns. of 0·01 g./l., O.D. (x) = (1) 0·312, (2) 0·277, (3) 0·330, (4) 0·450, (5) 0·442, (6) 0·237, (7) 0·521, (8) 0·385, (9) 0·660, (10) 0·338, (11) 0·346, (12) 0·316, (13) 0·349, (14) 0·622, (15) 0·608, (16) 0·332, (17) 0·325, (18) 0·110, (19) 0·223, (20) 0·268, (21) 0·253, (22) 0·186, (23) 0·194, (24) 0·285, (25) 0·361, (26) 0·169, (27) 0·320. For 0·004 g./l., O.D. (x) = (28) 0·110, (29) 0·061. Also, O.D. (x) = (30) 3·48 at 0·20 g./l., (31) 0·084 at 0·0056 g./l., (32) 0·346 at 0·0348 g./l., (33) 1·250 at 0·1419 g./l., (34) 1·490 at 0·1682 g./l., (35) 0·922 at 11·92 g./kg.,‡ (36) 0·860 at 5·03 g./kg.,‡ (37) 0·832 at 4·35 g./kg.,‡ (38) 0·062 at 0·0033 g./l., (39) 0·283 at 0·0185 g./l., (40) 1·105 at 0·432 g./l., (41) 0·074 at 0·0034 g./l., (42) 0·382 at 0·0191 g./l., (43) 1·340 at 0·1063 g./l.

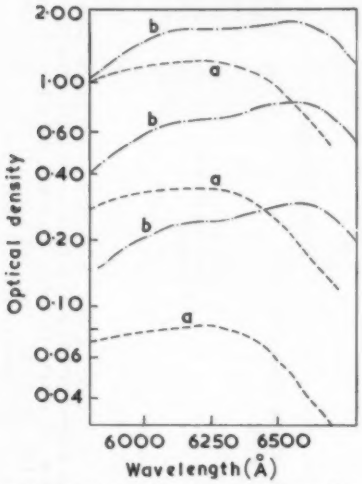
‡ 0·0015 in. gauge Cellophane film. The molar extinction coefficients of these dyes in cellulose appear to be 2—3 times their values in water.

§ See Cameron and Giles, *J.*, 1957, 3140.

¶ x-Band flatter than at lower optical densities.

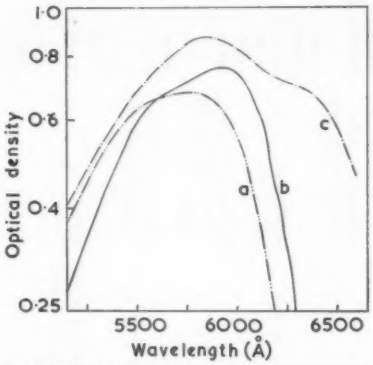
in silver halide–gelatin emulsions (see, *e.g.*, refs. 2*c*,*f*), little previous work on the occurrence of *x*- and *y*-bands in spectra of *adsorbed* dyes has been reported. In connection with a study of the photo-tendering properties of anthraquinone dyes Moran and Stonehill [7] described

FIG. 1. *Absorption spectra of a (direct cotton) bisazo-dye* (C.I. 24,410, *Sky Blue FF*) *in various media.*



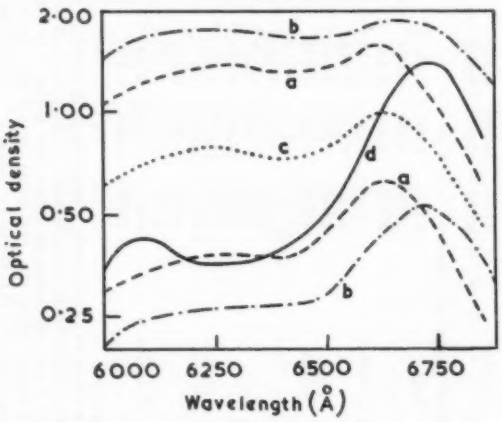
a, *Water*; b, *dyed regenerated cellulose film.*

FIG. 2. *Absorption spectra of a (direct cotton) bisazo-dye* (C.I. 24,140) *in various media.*



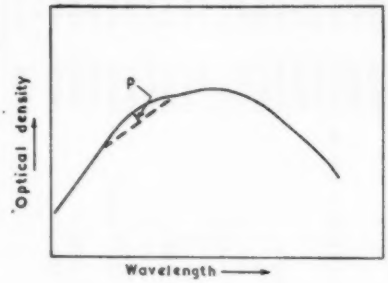
a, *Methanol*; b, *pyridine*; c, *dyed regenerated cellulose film.*

FIG. 3. *Absorption spectra of a reactive dye* (*Procion Brilliant Blue* H7G) *in various media.*



a, *Water*; b, *dyed regenerated cellulose film*; c, *alkaline solution, after boiling*; d, *pyridine.*

FIG. 4. *Illustrating the method of estimating the position of a subsidiary absorption peak. The peak is at the intersection of the curve with the perpendicular* p. *This method was checked by graphically adding peaks of different heights.*



the *x*- and *y*-bands in spectra of vat dyes dyed on cellulose acetate films, but they did not investigate the effect of changing the concentration.

We have examined the visible absorption spectra of dyes of various chemical classes, in solution in water and other solvents and adsorbed in transparent films (see Table 1). In particular the changes in the shapes of the absorption spectra with concentration have

been recorded, in terms of the ratio of heights of the two bands that appear in almost all cases (cf. Figs. 1—3). The significance of the results was analysed statistically (see Appendix). The conclusions may be summarised thus:

(i) Most dyes of all classes have two absorption bands in the visible region, which we tentatively identify with Lewis and Calvin's x and y bands,* because they are close together and because increase in dye concentration, either in solution or adsorbed in solid films, or change from a non-associating solvent (*e.g.*, methanol or pyridine) to an associating one (*e.g.*, water) almost always increases the height of the band of shorter wave-length relative to that of longer wavelength (in only a very few cases the height remains constant, or decreases very slightly). In many cases the bands are so close as to make one of them difficult to locate with precision; it appears as a very slight bulge on the short-wave side (occasionally on the long-wave side) of the main peak: the approximate position of this type of band was estimated as shown in Fig. 4.

(ii) Both bands persist in all media, but there is in most cases a " solvatochromic " shift of both bands with change of solvent.†

(iii) The similarity in behaviour with increase in concentration of each dye in solution or adsorbed in films is evidence that the adsorbed dye is at least partly aggregated. This confirms the result of the examination of " Beer's law curves " of dyed films reported earlier.[1]

(iv) The change in height of the y-band relative to that of the x-band with increase in concentration is small (*ca.* 5% for a 100-fold increase in concentration).

(v) The main (x) band of many dyes shifts to longer wavelengths when the dye is adsorbed on cellulose. In the adsorbed state the dye molecules are probably aligned parallel to the cellulose chains, and separated therefrom by a layer of water molecules.[9] Krasovitskii and Pereyaslova[10] found that $\lambda_{max.}$ for benzidine direct cottton dyes is frequently much higher on regenerated cellulose sheet than in solution, and attributed this to increased conjugation in the dye molecule, caused by improved planarity.

Reactive Dyes.—These recently introduced dyes[11] differ from most others in forming a covalent bond with the fibre molecule itself. The present results show that they are aggregated in the solid substrate, a conclusion previously reached from a study of light-fading rates.[12] Their intermolecular forces are therefore sufficiently powerful to cause aggregation even when one point on the dye molecule is covalently attached to the fibre molecular chain. During the reaction with the fibre the system is, of course, in an aqueous medium, and the fibre molecules accessible to dye will be solvated by water and flexible enough to accommodate themselves to the positions taken up by the aggregated dye molecules.

Experimental

Dyes.—These were laboratory or commercial products recrystallised three times from 3 : 2 v/v ethanol–water; after two recrystallisations the apparent molar extinction coefficients did not increase, and this was taken to indicate complete removal of inorganic impurities. The two azo-pyrazolone dyes were obtained in an already purified form. Malachite Green was

* The azo-dyes used are *o*-aminoazo- or *o*-hydroxyazo-compounds and cannot readily show azo–quinone imine or *cis–trans* changes. This was confirmed by examination of Orange II (sulphanilic acid → 2-naphthol) solutions: the $x : y$ band ratio does not change with variation in pH or on prolonged intense illumination.

† Kundt's rule[8] is that an increase in refractive index of solvent causes the absorption waveband to move to longer wavelengths. It is not always obeyed, and opposite effects are sometimes found amongst dyes of close similarity of structure. *E.g.*, Sky Blue FF (C.I. 24,410) obeys the rule in water and pyridine, but Benzopurpurine (C.I. 23,500) behaves in the opposite sense.

[8] Kundt, *Ann. Phys. Chem.*, 1878, **4**, 34.
[9] Giles and Hassan, *J. Soc. Dyers and Colourists*, 1958, **74**, 846.
[10] Krasovitskii and Pereyaslova, *Doklady Akad. Nauk S.S.S.R.*, 1954, **98**, 71; through *J. Soc. Dyers and Colourists*, 1955, **71**, 193.
[11] Vickerstaff, *J. Soc. Dyers and Colourists*, 1957, **73**, 237.
[12] Baxter, Giles and Lewington, *J. Soc. Dyers and Colourists*, 1957, **73**, 386.

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recrystallised twice from dilute hydrochloric acid. Distilled water was used for solutions for spectrophotometric measurements.

As controls for the cellulose films dyed with reactive dyes, dye solutions which had been boiled with alkali were employed. Alkali-boiling in absence of cellulose replaces the reactive chlorine atoms in the dye molecule by hydroxy-groups. In presence of cellulose the chlorine atoms are replaced by the ether link to the cellulose.

Ageing Effects, etc.—To prepare the aqueous solutions, the dye was first dissolved in a minimum of distilled water (cold for most dyes, boiling for a few of difficult solubility, *e.g.*, metal-complex dyes) and then diluted, as required, with cold water. Readings were then taken as soon as possible, usually within 30 min. of dilution. Tests were, however, made to determine whether there are any ageing effects, by examining the solutions (kept cold) at different periods up to 24 hr. With sulphonated dyes there was no change, except in one or two cases, where, over a period of several hours, the $y:x$ peak ratio increased by $<2\%$. The metal-complex dye solutions, however, which had been prepared by diluting the hot solution, showed a slight decrease in aggregation with time; the weakest solutions changed at the lowest rate. Thus a weak solution of Irgalan Orange RL with optical density 0·119 at 4800 Å decreased in $y:x$ ratio by about 15% over 24 hr.

To discover whether any of the spectral changes recorded could be caused by traces of metal ions, two dyes (C.I. 18,050, 24,410) were examined in 0·1% aqueous ethylenediamine-tetra-acetic acid solution. The spectra were the same as in water.

Preparation of Films.—The methods have been described.[1]

Instruments.—Unicam S.P. 500 and S.P. 600 spectrophotometers were used, by one operator.

The authors thank Professor P. D. Ritchie, F.R.S.E., for his encouragement and interest, and British Cellophane Ltd., Geigy Ltd., Imperial Chemical Industries Limited, Dyestuffs Division, and Sandoz Ltd. for the gift of materials.

Appendix

By D. Smith

To determine the significance of the optical-density ratios which form the basis of the present work, one dye (C.I. 18,050) was examined at three concentrations, the ratios of optical density at the two $\lambda_{max.}$ for each solution being determined three times. The whole operation was repeated by four different operators (S.P. 500 instrument). The results are shown in Table 2.

Table 2. *Replication results.*

Operator	A		B		
Concn.	Ratio *	Sum	Ratio	Sum	
a	1·067, 1·067, 1·064	3·198	1·058, 1·059, 1·062	3·179	
b	0·987, 0·985, 0·987	2·959	0·987, 0·987, 0·987	2·961	
c	0·970, 0·955, 0·955	2·880	0·969, 0·970, 0·985	2·924	
Total		9·037		9·064	
Operator	C		D		
Concn.	Ratio	Sum	Ratio	Sum	Total
a	1·079, 1·079, 1·079	3·237	1·055, 1·056, 1·056	3·167	12·781
b	0·983, 0·983, 0·985	2·951	0·978, 0·963, 0·970	2·911	11·782
c	0·952, 0·968, 0·953	2·873	0·955, 0·955, 0·955	2·865	11·542
Total		9·061		8·943	36·105

* Optical-density ratio, *y*-band/*x*-band maximum.

The analysis of variance gives $\sigma_0^2 = 0{\cdot}000025$ and hence the standard deviation for each ratio is $\pm 0{\cdot}005$. Therefore, the average percent error of each ratio is $\pm 0{\cdot}5$.

To find if the difference $(x_1 - x_2)$ in the ratio for two concentrations of a dye is significant at the 5% level, when the x's are the average of two readings, the t-test can be used Thus,

$$t = \frac{x_1 - x_2}{\left(\frac{\sigma_0^2}{2} + \frac{\sigma_0^2}{2}\right)} = \frac{x_1 - x_2}{\sigma_0} \text{ with 24 degrees of freedom}$$

At the 5% level of significance the difference in ratios is significant if $t \geqslant 2{\cdot}06$.

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Therefore, x_1 is significantly different from x_2 if $(x_1 - x_2) \geqslant \sigma_0 t \geqslant 0{\cdot}005 \times 2{\cdot}06 \geqslant 0{\cdot}01$, which is approximately the smallest difference recorded in Table 1.

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[*Received, July 4th*, 1960.]

238. *The Photoisomerisation of 3β-Acetoxylanosta-5,8-dien-7-one.*

By D. H. R. Barton, J. F. McGhie, and M. Rosenberger.

The ring B dienone, 3β-acetoxylanosta-5,8-dien-7-one, has been photoisomerised to an umbellulone. Two separate series of degradational experiments have excluded a number of possible formulæ and have provided strong support for formula (IV; R = Ac) for the photoisomer. Rotatory dispersion evidence for the stereochemistry of (IV; R = Ac) has been obtained.

In 1954 Dr. E. L. Wheeler, working at Birkbeck College in collaboration with one of us (D H. R. B.), noted that 3β-acetoxylanosta-5,8-dien-7-one was easily converted by ultraviolet light into an isomer characterised by its spectral properties as an umbellulone. In the meantime the photoisomerisation of santonin (II) to lumisantonin (III) has been thoroughly studied [1,2] and the stereochemical course of the reaction elucidated.[3] It has also been shown that steroidal 1,4-dien-3-ones rearrange easily on irradiation,[4,5] although the structural change induced is quite different from that implied in the sequence (II ⟶ III). The attachment of a 4-methyl group so that the chromophore reverts to that present in santonin (II) leads, however, to a santonin-type rearrangement.[6] We consider that each case of photoisomerisation of a cyclohexadienone has to be considered on its own merits. Thus, if the change (II ⟶ III) is taken as general, the constitution (IV; R = Ac) can be written for the photoisomer of the dienone (I). The mere formation of an umbellulone, however, does not exclude formulæ such as (V) and (VI), or even (IX), as well as more complex rearrangements as yet unexemplified.[5] In the event, we were able to show that (IV; R = Ac) is indeed the correct representation of the photoisomer and for clarity we shall use this formula in the sequel.

The photoisomer gave the corresponding alcohol (IV; R = H) on mild alkaline hydrolysis. Acetylation of the alcohol gave back the starting acetate, and oxidation by chromic acid furnished the derived ketone (VII), further characterised as its dioxime and by condensation with benzaldehyde to afford the benzylidene derivative (VIII). Under the influence of hydrogen chloride in chloroform solution the umbellulone (VII) rearranged to an isomer (X), characterised as its benzylidene derivative (XI). Although the acid-catalysed rearrangements of umbellulones can, in principle, be very complex, the relationship between (VII) and (X) was shown to be as simple as indicated because the benzylidene derivative (XI) could also be derived from (VIII) by rearrangement with alkali (VIII; see arrows).

The βγ-unsaturated nature of the diketone (X), shown by the ultraviolet absorption spectrum of its derivative (XI) and by ozonolysis of the latter to give the yellow α-diketone (XII) with a characteristic spectrum, was thoroughly confirmed by stepwise degradation. Reaction of the diketone (X) with osmium tetroxide and cleavage of the product with lead tetra-acetate furnished the hydroxymethylene-triketone (XIII), the functional groups of which were indicated by its spectral properties. Oxidation of this triketone (XIII)

[1] Barton, de Mayo, and Shafiq, *Proc. Chem. Soc.*, 1957, 205; *J.*, 1958, 140; see also Cocker, Crowley, Edward, McMurry, and Stuart, *J.*, 1957, 3416.
[2] Arigoni, Bosshard, Bruderer, Büchi, Jeger, and Krebaum, *Helv. Chim. Acta*, 1957, **40**, 1732.
[3] Barton and Gilham, *Proc. Chem. Soc.*, 1959, 391; *J.*, 1960, 4596.
[4] Barton and Taylor, *J. Amer. Chem. Soc.*, 1958, **80**, 244; *J.*, 1958, 2500.
[5] Dutler, Bosshard, and Jeger, *Helv. Chim. Acta*, 1957, **40**, 494.
[6] Weinberg, Utzinger, Arigoni, and Jeger, *Helv. Chim. Acta*, 1960, **43**, 236.

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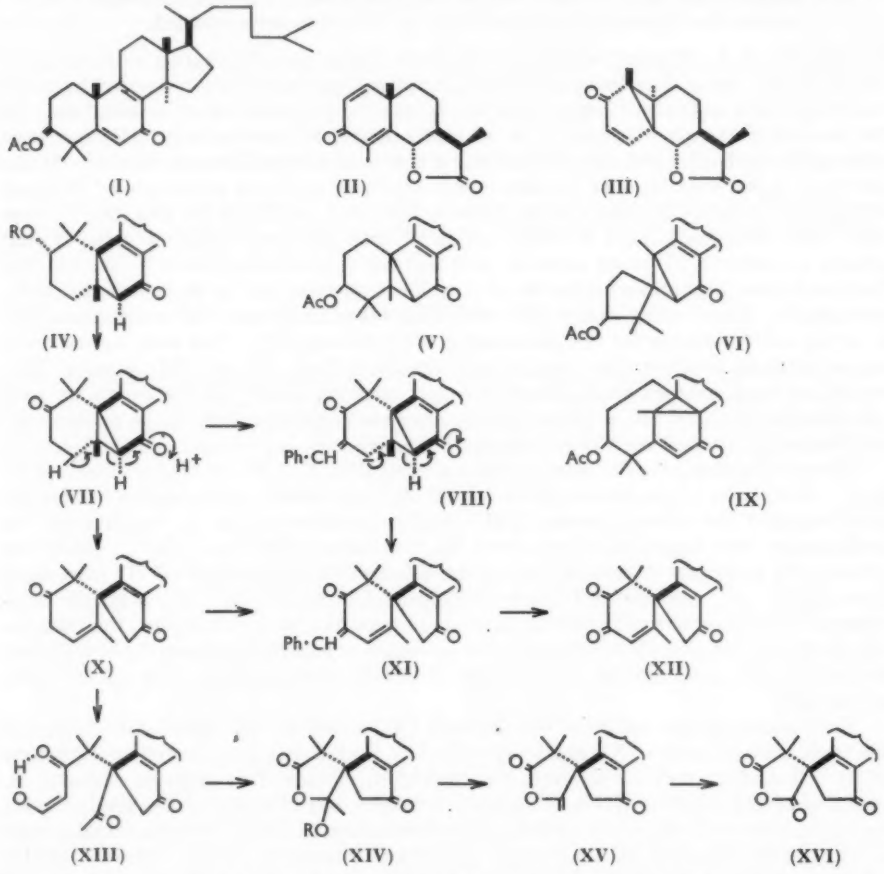
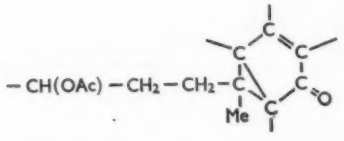
with chromic acid gave the pseudo-acid (XIV; R = H), which could be acetylated to the derivative (XIV; R = Ac). The latter had a characteristic infrared spectrum indicating a γ-lactone group and an acetoxyl residue related to each other as in (XIV; R = Ac). Pyrolysis of this acetate (XIV; R = Ac) proceeded smoothly to give acetic acid and the methylene-lactone (XV). Ozonolysis of the latter afforded formaldehyde and the substituted succinic anhydride (XVI). The last two compounds had infrared spectra which were fully in accord with the proposed structures. All the compounds (X)—(XVI) showed ultraviolet and infrared absorption in agreement with the presence of a fully substituted cyclopentenone grouping. This series of experiments shows that the photoisomer (IV; R = Ac) contains the sequence indicated in part formulation (XVII). Formulæ (V), (VI), and (IX) are, therefore, excluded.

The action of hydrogen chloride in chloroform upon the acetate (IV; R = Ac) took a different course (XVIII; R = Ac; see arrows) from that observed with the ketone (VII) (see

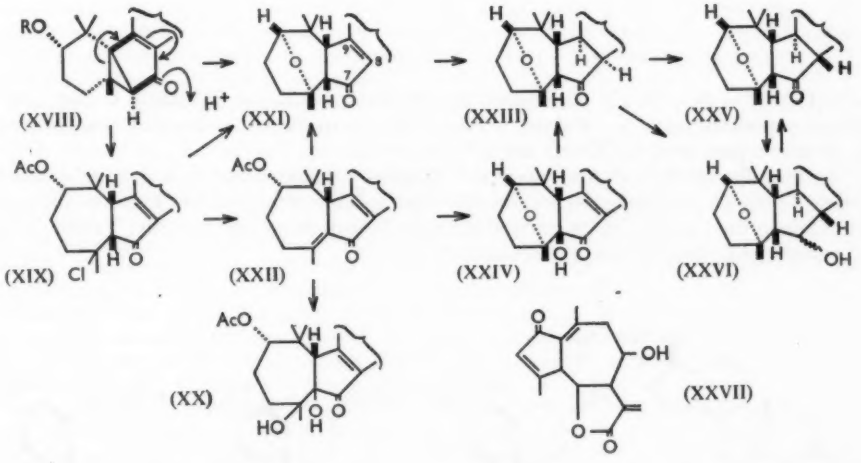


above). There resulted a hydrochloride which is best formulated as (XIX) on the basis of the following evidence. It contained a cyclopentenone chromophore and on attempted alkaline hydrolysis furnished an oxide (XXI). The latter retained the same chromophore and, from its nuclear magnetic resonance spectra, had one hydrogen attached to carbon bearing oxygen and no vinyl hydrogen atoms. This oxide (XXI) was also obtained when the

alcohol (XVIII; R = H; see arrows) was treated with hydrogen chloride in the same way. Heating the hydrochloride (XIX) in acetic acid gave a dienone (XXII) with an unusual absorption spectrum [$\lambda_{max.}$ 271 mμ (ε 12,600)]. This is similar to the spectrum of lactucin (XXVII) [$\lambda_{max.}$ 257 mμ (ε 14,000)] where a comparable chromophore is known to be present.[7] The dienone had no vinyl hydrogen atom (nuclear magnetic resonance spectrum) but had one hydrogen atom attached to carbon bearing oxygen and one methyl group attached to vinylic carbon in *cisoid* conformation (τ = 7·72). These results are fully in accord with formula (XXII). On mild treatment with alkali the dienone also gave the oxide (XXI). A comparable bridging of a seven-membered ring by hydroxyl addition to the β-position of an enone system has already been observed in the chemistry of geigerin.[8] The hydrochloride (XIX) was not reduced by activated zinc or by chromous chloride, results which are in accord with halogen β- rather than α- to the ketone group. Reduction of the oxide (XXI) with lithium in ammonia gave a cyclopentanone (XXIII). Again the retention of the oxide function shows[9] that it must be β-, not α-, with respect to the ketone group. This cyclopentanone (XXIII) had one (or both) of its α-asymmetric centres in an unstable configuration for treatment with base, or with refluxing acetic



(XVII)



(XVIII) (XXI) (XXIII) (XXV)
(XIX) (XXII) (XXIV) (XXVI)
(XX)

(XXVII)

anhydride–sodium acetate, gave a more stable isomer (XXV). Reduction of either isomer (XXIII) or (XXV) with sodium and alcohol gave the same derivative (XXVI) from which the isomer (XXV) could be obtained by oxidation with chromic acid. The dienone (XXII) with osmium tetroxide gave the glycol (XX) which, in agreement with its formulation as ditertiary, resisted acetylation. Reaction with per-acid gave the hydroxy-oxide (XXIV) which was resistant to acetylation and oxidation, and which on reduction with lithium and ammonia furnished the keto-oxide (XXIII) already described above. This experiment confirms the view that the tertiary hydroxyl group of compound (XXIV) is

[7] Barton and Narayanan, *J.*, 1958, 963.
[8] Barton and Levisalles, *J.*, 1958, 4518.
[9] Cf. Chapman, Elks, Phillipps, and Wyman, *J.*, 1956, 4344.

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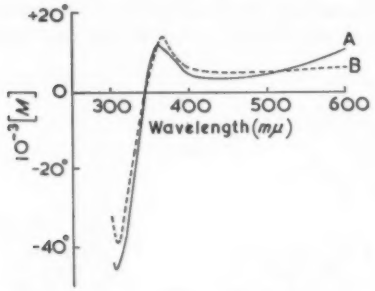
α- with respect to the ketone group and that the ethereal ring is attached β- as already formulated.

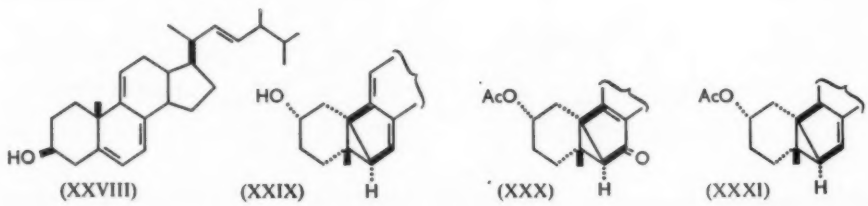
The stereochemistry [3] of the santonin ⟶ lumisantonin rearrangement represents an inversion of configuration at the angular 10-methyl group. If the same type of inversion is assumed for the rearrangement of 3β-acetoxylanosta-5,8-dien-7-one, then the stereochemistry already given in (IV; R = Ac) would follow. Now, recently the stereochemistry of the dehydroergosterol (XXVIII) ⟶ photodehydroergosterol [10] (XXIX) rearrangement has been represented as in these formulæ.[11] If, therefore, photodehydroergosterol could be converted into the umbellulone (XXX) a good model for the rotatory dispersion curve [12] expected for (IV; R = Ac) would be available. To this end tetrahydrophotodehydroergosterol acetate (XXXI) was oxidised with chromium trioxide in pyridine to furnish the desired umbellulone (XXX). This oxidation is exactly comparable with prior example.[10] The rotatory dispersion curves in methanol solution of compounds (XXX)



Optical rotatory dispersion of (A) *compound* (XXX) *and* (B) *the photo-product* (IV; R = Ac).

and (IV; R = Ac), kindly determined by Professor W. Klyne (Westfield College), were almost superimposable (see Figure). This is strong support for identical configurations as already represented in (XXX) and (IV; R = Ac).

In formulæ (XIX)—(XXVI) we have assigned configurations to a number of asymmetric centres. The assignments are intended to illustrate that the formulæ proposed will explain the chemical facts configurationally as well as constitutionally. They do not represent rigidly established stereochemistry.



The acetoxyl group of compounds (XIX), (XX), and (XXII) is of defined configuration. In the reaction of (XXII) with per-acid it is reasonable to accept that the ethereal oxygen bridge is formed *trans* to the hydroxyl group. Furthermore, models show that this easy bridging reaction would not be expected unless the ring fusion of the cycloheptane and

[10] Barton and Kende, *J.*, 1958, 688.
[11] Barton, Bernasconi, and Klein, *J.*, 1960, 511.
[12] Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co. Inc., New York, 1960; Klyne in "Advances in Organic Chemistry," Vol. I, p. 239, Interscience Publ. Inc., New York, 1960 (eds. Raphael, Taylor, and Wynberg).

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cyclopentenone rings in (XXIV) were *cis*, as written into the formula. The stereochemistry of (XIX) and (XXI) is given with this assignment in mind, and with the supposition that both compounds are formed under equilibrating conditions with the *cis*-fusion favoured. It is true that in the perhydroazulene series the *trans*-fusion of the rings predominates at equilibrium,[13] but when three trigonal atoms are introduced into the five-membered ring the reverse is surely to be expected. Especially is this so if there is also an oxygen bridge across the seven-membered ring as in (XXI). The additional asymmetric configurations at positions 8 and 9 in (XXIII), (XXV), and (XXVI) represent our estimate from models of the more stable configuration at position 9 in all three cases and our interpretation of the possible relative configurations at position 8.

In the Experimental section there is recorded the preparation of several toluene-*p*-sulphonates and methanesulphonates which were employed in abortive degradational experiments.

In a letter dated June 24th, 1960, Professor K. Tsuda of the Institute of Applied Microbiology of the University of Tokyo has kindly informed us that he and his colleagues have also prepared the photoisomer of 3β-acetoxylanosta-5,8-dien-7-one and have characterised it by conversion into the corresponding ketone.

Experimental

Rotations were determined for $CHCl_3$ solutions in a 4 dm. tube except where denoted ($l = 0{\cdot}5$). Ultraviolet absorption spectra were taken for EtOH solutions on the Unicam S.P. 500 spectrophotometer. Infrared spectra were taken for Nujol mulls. Alumina for chromatography was acid-washed, neutralised, reactivated, and then standardised according to Brockmann's scale. Solvents for chromatography were dried and redistilled. Light petroleum refers to a fraction of b. p. 40—50° unless stated otherwise. Kiliani's chromic acid mixture was prepared from sodium dichromate (60 g.) in water (270 ml.) to which concentrated sulphuric acid (80 g.) was added.

Nuclear magnetic resonance spectra were kindly determined and interpreted by Drs. L. M. Jackman and J. W. Lown to whom we express our best thanks. The spectra were taken for $CDCl_3$ solution on a Varian Associates spectrometer model V 4311 at a fixed frequency of 56·445 Mc./sec. Line positions were measured by the conventional side-band technique with a Muirhead Decade oscillator (Model D 695-A), tetramethylsilane being added as internal standard. For general information on the definition of τ and other symbols see ref. 14.

3β-*Acetoxylanosta*-5,8-*dien*-7-*one*.—3β-Acetoxylanost-8-en-7-one [15] (67 g.) in acetic acid (1·25 l.) was treated slowly with bromine (7·9 ml., 1·1 mol.) in acetic acid (250 ml.) at room temperature. The reaction was initiated by the addition of a 50 w/v solution (1·0 ml.) of hydrogen bromide in acetic acid. The bromine was rapidly consumed. Nitrogen was passed through the solution at room temperature for 6 hr. to remove the excess of hydrogen bromide, and then the solution was poured into water, 5% aqueous sodium sulphite solution (500 ml.) was added, and the solid was filtered off. The precipitate was taken up into benzene and washed with water (2 × 200 ml.), 2N-sodium carbonate (200 ml.), and then water again. The benzene was removed *in vacuo*. Crystallisation from chloroform–methanol gave 3β-acetoxylanosta-5,8-dien-7-one (53·5 g.), m. p. 186—188°, $[\alpha]_D$ −13° (*c* 1·05). Barton and Thomas [16] record m. p. 186—188°, $[\alpha]_D$ −14°.

Irradiation of 3β-*Acetoxylanosta*-5,8-*dien*-7-*one* (with Dr. E. L. Wheeler).—The dienone (10 g.) in absolute ethanol (500 ml.) was irradiated in a Pyrex flask at reflux under oxygen-free nitrogen by a 125 w mercury lamp for 45 min. ($[\alpha]_D$ −13° ⟶ $[\alpha]_D$ +40° to +50°). Longer irradiation produced larger rotational changes but lower net yields. Removal of the solvent *in vacuo* and crystallisation from methanol (350 ml.) furnished unchanged dienone (4—6 g.). The filtrate was concentrated to 300 ml. and seeded with the desired product. Leaving it for 2 days (10 days without seeding) gave the *umbellulone* (IV; R = Ac) (1·1 g.) as plates,

[13] Ayres and Raphael, *J.*, 1958, 1779.
[14] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.
[15] Birchenough and McGhie, *J.*, 1950, 1249.
[16] Barton and Thomas, *J.*, 1953, 1842.

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m. p. 146—148°, resolidifies, remelts at 158—159°, $[\alpha]_D$ +189° (*c* 1·59; *l* = 0·5), $\lambda_{max.}$ 205, 233, and 280 mμ (ε 7500, 6400, and 3500 respectively), $\nu_{max.}$ 1740 (OAc), 1687 and 1612 (umbellulone) (Found: C, 79·45; H, 10·5. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·45%). This acetate (500 mg.) in methanol (40 ml.) was treated with potassium hydroxide (500 mg.) in methanol (10 ml.) under reflux for 2 hr. Addition of acetic acid (1 ml.), removal of the solvent *in vacuo*, and working up in the usual way gave, on crystallisation from aqueous methanol, the desired *alcohol* (IV; R = H) as needles (442 mg.), m. p. 163—165°, $[\alpha]_D$ +162° (*c* 0·73, $\lambda_{max.}$ 236 and 279 mμ (ε 6100 and 3100 respectively), $\nu_{max.}$ 3559 (OH), 1663, and 1609 (umbellulone) cm.$^{-1}$ (Found: C, 81·9; H, 11·0. $C_{30}H_{48}O_2$ requires C, 81·75; H, 11·0%). Treatment with pyridine–acetic anhydride overnight at room temperature gave back the starting acetate (m. p. and mixed m. p.).

This alcohol (5·6 g.) in benzene–acetic acid (4 : 1; 500 ml.) was stirred for 1 hr. at room temperature with Kiliani chromic acid mixture (55 ml.). Destruction of the excess of oxidant with 2% sodium hydrogen sulphite solution and working up in the usual way gave the desired *ketone* (VII) in nearly quantitative yield. Recrystallised from chloroform–methanol as needles, this had m. p. 204—206°, $[\alpha]_D$ +152° (*c* 0·88), $\lambda_{max.}$ 227 and 279 mμ (ε 6500 and 3200 respectively), $\nu_{max.}$ 1703 (cyclohexanone), 1684 and 1620 (umbellulone) cm.$^{-1}$ (Found: C, 82·2; H, 10·9. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·85%). This diketone (500 mg.) was treated with hydroxylamine hydrochloride (500 mg.) in pyridine (20 ml.) at 100° for 3 hr. Working up in the usual way and crystallisation from benzene furnished the *dioxime* as cubes (507 mg.), m. p. 265—266° (decomp.), $[\alpha]_D$ +200° (*c* 0·51), $\lambda_{max.}$ 265 mμ (ε 9000), $\nu_{max.}$ 3257 and 3101 (OH) and at 1634 and 1597 (C=N) cm.$^{-1}$ (Found: C, 76·75; H, 10·65. $C_{30}H_{48}N_2O_2$ requires C, 76·85; H, 10·3%).

Condensation of the Ketone (VII) *with Benzaldehyde*.—The ketone (VII) (300 mg.) in 0·1N-ethanolic potassium hydroxide (30 ml.) was treated with benzaldehyde (750 mg.; redistilled) in the dark at room temperature for 16 hr. under oxygen-free nitrogen. The desired *benzylidene ketone* (VIII) crystallised out (264 mg.) during this time. Working up the mother-liquors in the usual way gave additional material (40 mg.). Recrystallisation of the combined product from ethyl acetate–methanol gave the compound as needles (280 mg.), m. p. 196—197°, $[\alpha]_D$ +77° (*c* 0·81), $\lambda_{max.}$ 224 and 290 mμ (ε 13,700 and 22,800 respectively) (Found: C, 84·35; H, 9·6. $C_{37}H_{50}O_2$ requires C, 84·35; H, 9·55%). The ultraviolet addition curve of 2-benzylidenelanost-8-enone [17] with the ketone (VII) showed $\lambda_{max.}$ 225 and 290 mμ (ε 14,500 and 20,600 respectively).

Treatment of the Ketone (VII) *with Hydrogen Chloride*.—The ketone (VII) (2 g.) in chloroform (200 ml.), saturated with dry hydrogen chloride, was left at room temperature in the dark for 2 days [ultraviolet control; until constant $\lambda_{max.}$ 245 mμ (ε 12,000)]. More chloroform (200 ml.) was added and the solution worked up in the usual way. The product was taken up in acetic acid (200 ml.), heated under reflux for 10 min., and then extracted with benzene. Working up in the usual way gave, after crystallisation from methanol, the isomerised *ketone* (X) (1·55 g.) as plates, m. p. 141—143°, $[\alpha]_D$ +202° (*c* 0·25), $\lambda_{max.}$ 245 mμ (ε 13,500), $\nu_{max.}$ 1706 (cyclohexanone), 1684 (sh), and 1623 (cyclopentenone) cm.$^{-1}$ (Found: C, 82·35; H, 10·45. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·55%).

This ketone (1·5 g.) in 0·1N-ethanolic potassium hydroxide (100 ml.) was treated with benzaldehyde (3·6 g.; redistilled) in the dark under oxygen-free nitrogen at room temperature for 16 hr. Dilution with aqueous 2N-sodium hydrogen sulphite, extraction into ether, and working up in the usual way gave the *benzylidene derivative* (XI). This crystallised from ethyl acetate–methanol as needles (1·41 g.), m. p. 145—147°, $[\alpha]_D$ +245° (*c* 1·02), $\lambda_{max.}$ 234 and 323 mμ (ε 18,000 and 18,500 respectively) (Found: C, 84·35; H, 9·6. $C_{37}H_{50}O_2$ requires C, 84·6; H, 9·55%).

This benzylidene derivative was also obtained by the following two routes. (*a*) The benzylidene ketone (VIII) (20 mg.) in chloroform (10 ml.) was treated with dry hydrogen chloride as above, but the refluxing with acetic acid was omitted. This furnished the isomerised benzylidene ketone (XI) (15 mg.), identified by m. p. and mixed m. p. (*b*) The benzylidene ketone (VIII) (150 mg.) in 2·5% ethanolic potassium hydroxide (25 ml.) was heated under oxygen-free nitrogen under reflux for 15 min. Dilution with aqueous N-hydrochloric acid, extraction with ether, and working up in the usual way furnished a gum (150 mg.) which was chromatographed over alumina (Grade V; 6 g.). Elution with benzene–light petroleum (1 : 9 and 1 : 4) and crystallisation with methanol gave the rearranged benzylidene ketone

[17] Barton, Head, and May, *J.*, 1957, 935.

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(XI) (70 mg.), identified by m. p., mixed m. p., rotation {$[\alpha]_D$ +243° (*c* 0·20)}, and ultraviolet absorption.

Ozonolysis of the Benzylidene Ketone (XI).—The benzylidene ketone (XI) (1·0 g.) in dry ethyl acetate (150 ml.) was treated at −70° with ozone until there was a slight excess of oxidant [$\lambda_{max.}$ 324 mμ (ε 18,000 ⟶ <500)]. A stream of oxygen-free nitrogen was passed through the solution whilst it was allowed to warm to room temperature. Addition of water, removal of the ethyl acetate *in vacuo*, extraction with ether, and working up in the usual way gave, after several crystallisations from methanol, the yellow diketone (XII) as needles, m. p. 201—204°, $[\alpha]_D$ +436° (*c* 0·35), $\lambda_{max.}$ 242 mμ (ε 13,100), $\nu_{max.}$ 1761 and 1723 (α-diketone), 1692 (cyclopentenone), 1669 and 1620 (conjugated C=C) cm.$^{-1}$ (Found: C, 79·45; H, 9·65. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%).

Degradation of the Diketone (X).—The diketone (X) (5 g.) in pyridine (10 ml.) was treated with osmium tetroxide (4 g.) in pyridine (10 ml.) at room temperature in the dark for 4 days. The mixture was diluted with ether (500 ml.) and saturated with hydrogen sulphide (1 hr.). The black precipitate was removed and the ethereal solution worked up in the usual way. A portion of the crude product (96 mg.) was treated with lead tetra-acetate (200 mg.) in acetic acid (5 ml.). After 1 hr. (one " oxygen " uptake) ethylene glycol (1 ml.) was added, the mixture diluted with water and extracted with ether, and the extract worked up in the usual way. Crystallisation of the product from aqueous methanol gave the *hydroxymethylene compound* (XIII) (38 mg.) as needles, m. p. 178—180°, $[\alpha]_D$ +28° (*c* 0·27), $\lambda_{max.}$ 266 mμ (ε 18,000), $\lambda_{max.}$ (in 0·1% ethanolic KOH) 252 and 308 mμ (ε both 8600), $\nu_{max.}$ 3215 (OH), 1695 (Me ketone and cyclopentenone), 1647 (hydrogen-bonded ketone) and 1613 (C=C) cm.$^{-1}$ (Found: C, 76·6; H, 9·9. $C_{30}H_{46}O_4$ requires C, 76·55; H, 9·85%). The compound gave an immediate ferric reaction.

This hydroxymethylene compound (XIII) (256 mg.) in acetic acid (15 ml.) containing chromium trioxide (300 mg.) was kept for 1 hr. at room temperature (4 " oxygen " uptake). Dilution with 1% sodium hydrogen sulphite solution, extraction with ether, and working up in the usual way gave an acidic oil (145 mg.). Crystallised from aqueous methanol this furnished the *pseudo-acid* (XIV; R = H) (78 mg.), m. p. 193—195°, $[\alpha]_D$ +39° (*c* 0·297), $\lambda_{max.}$ 242 mμ (ε 10,000), $\nu_{max.}$ 3300 (OH), 1733 (ψ-acid C=O), and 1698 and 1623 (cyclopentenone) cm.$^{-1}$ (Found: C, 75·4; 75·65; H, 10·15, 10·15%; equiv., 480. $C_{28}H_{44}O_4$ requires C, 75·65; H, 9·95%; equiv., 444). Treatment with pyridine–acetic anhydride at room temperature for 3 days furnished the pseudo-acid *acetate* (XIV; R = Ac). Recrystallised from light petroleum (b. p. 60—80°), this formed needles, m. p. 199—200°, $[\alpha]_D$ +31° (*c* 0·338), $\lambda_{max.}$ 238—240 mμ (ε 12,000), $\nu_{max.}$ 1786 (exalted γ-lactone), 1770 (acetate of pseudo-acid), 1709 and 1620 (cyclopentenone) cm.$^{-1}$ (Found: C, 74·65; H, 9·65. $C_{30}H_{46}O_5$ requires C, 74·05; H, 9·55%).

This acetate (213 mg.) was heated at 280—300° for 5 min. under a stream of oxygen-free nitrogen. The nitrogen stream was led through 0·1N-aqueous sodium hydroxide which, on titration, showed the formation of 0·81 equiv. of acid. After titration the water was removed *in vacuo* and the residue (28·4 mg.) characterised as sodium acetate by its infrared spectrum and by conversion into *p*-bromophenacyl acetate (m. p. and mixed m. p.). The residue from the pyrolysis was chromatographed over alumina (Grade V; 10 g.). Elution with benzene–light petroleum mixtures followed by crystallisation from aqueous methanol afforded the *methylene lactone* (XV) as needles (88 mg.), m. p. 108—109°, $[\alpha]_D$ +140° (*c* 0·489), $\lambda_{max.}$ 242 mμ (ε 9600), $\nu_{max.}$ 1812 (exalted γ-lactone), 1707 and 1631 (cyclopentenone), and 1667 (vinyl ether) cm.$^{-1}$ (Found: C, 78·8; H, 9·9. $C_{28}H_{42}O_3$ requires C, 78·8; H, 9·9%).

This methylene lactone (XV) (63 mg.) in dry ethyl acetate (15 ml.) was ozonised at −70° until there was a slight excess of ozone. Addition of water, removal of the solvent *in vacuo*, and extraction into ether furnished, after three crystallisations from light petroleum, the *anhydride* (XVI), m. p. 132—132·5°, $[\alpha]_D$ +154° (*c* 0·153), $\lambda_{max.}$ 246 mμ (ε 9000), $\nu_{max.}$ 1845 and 1776 (succinic anhydride), 1709 and 1629 (cyclopentenone) cm.$^{-1}$ (Found: C, 75·5; H, 9·4. $C_{27}H_{40}O_4$ requires C, 75·65; H, 9·4%).

In a second ozonolysis of the methylene lactone (70 mg.) the product was steam-distilled into aqueous dimedone to give the formaldehyde derivative (25 mg.), identified by m. p., mixed m. p., and crystal form.

Action of Hydrogen Chloride on the Acetate (IV; R = Ac).—The acetate (IV; R = Ac) (3 g.) in chloroform (300 ml.) was saturated with dry hydrogen chloride and left in the dark at room temperature for 20 hr. Addition of more chloroform (500 ml.), working up in the

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usual way, and crystallisation from methanol gave the ***chloride*** (XIX) (1·87 g.) as needles, m. p. 179—181°, $[\alpha]_D$ +3° (*c* 4·15), $\lambda_{max.}$ 246 mμ (ε 11,000), $\nu_{max.}$ 1728 (OAc), 1686 and 1622 (cyclopentenone) cm.$^{-1}$ (Found: C, 74·05; H, 9·75; Cl, 6·9. $C_{32}H_{51}ClO_3$ requires C, 74·0; H, 9·9; Cl, 6·85%). This chloride was recovered unchanged (m. p. and mixed m. p.) after attempted reduction with excess of chromous chloride and also with activated zinc dust in benzene–methanol under reflux.

The chloride (80 mg.) in ethanol (7 ml.) and benzene (3 ml.) was treated with potassium hydroxide (100 mg.) in ethanol (2·5 ml.) at room temperature in the dark for 16 hr. under oxygen-free nitrogen. Dilution with 2N-aqueous hydrochloric acid, extraction with ether, and working up in the usual way furnished the *oxide* (XXI). Recrystallised from methanol as needles, this had m. p. 177—178°, $[\alpha]_D$ 94° (*c* 1·64; *l* = 0·5), $\lambda_{max.}$ 245 mμ (ε 10,000), $\nu_{max.}$ 1682 and 1628 (cyclopentenone) (Found: C, 81·6; H, 10·8. $C_{30}H_{48}O_2$ requires C, 81·75; H, 11·0%). This oxide was recovered unchanged after treatment with hydrogen chloride in chloroform, with pyridine–acetic anhydride, and with Kiliani chromic acid mixture at room temperature. It also resisted reduction with chromous chloride, with zinc dust in refluxing acetic acid, or with lithium amalgam, acetylation with sodium acetate–acetic anhydride under reflux, and treatment with boiling methanolic potassium hydroxide.

The oxide was also obtained in the following manner. The photo-isomer alcohol (IV; R = H) (28 mg.) in chloroform (5 ml.) was saturated with dry hydrogen chloride and kept at room temperature for 2 hr. (ultraviolet control). Working up in the usual way and crystallisation from methanol gave the oxide (XXI) (15 mg.), identified by m. p., mixed m. p. and rotation {$[\alpha]_D$ +89° (*c* 1·10; *l* = 0·5)}.

Reduction Experiments with the Oxide (XXI).—The oxide (XXI) (1·0 g.) in dry tetrahydrofuran (150 ml.) was added during 10 min. to dry, redistilled ammonia (250 ml.) containing lithium (100 mg.) at the b. p. of liquid ammonia. Further lithium was added to maintain a slight excess. The mixture was stirred for a further 10 min., ammonium chloride (5 g.) was added, and the solution allowed to warm to room temperature. Ether-extraction and working up in the usual way gave the *dihydro-oxide* (XXIII). This crystallised from methanol as needles (250 mg.), m. p. 202—204°, $[\alpha]_D$ +121° (*c* 0·46), $\nu_{max.}$ 1728 (cyclopentanone) cm.$^{-1}$ (Found: C, 81·45; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). This dihydro-oxide (XXIII) (50 mg.) in ethanol (10 ml.) was further reduced by heating it under reflux with addition of sodium (excess). Dilution with water and working up in the usual way gave, after crystallisation from aqueous methanol, the *alcohol* (XXVI) as needles (25 mg.), m. p. 206—208°, $[\alpha]_D$ +60° (*c* 0·092), depressed in m. p. on admixture with starting material (Found: C, 81·6; H, 12·15. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

The dihydro-oxide (XXIII) (19·4 mg.) was refluxed with 5% methanolic potassium hydroxide (10 ml.) for 1 hr. under oxygen-free nitrogen. Dilution with 2N-aqueous hydrochloric acid and working up in the usual way gave the epi-*dihydro-oxide* (XXV) as needles (12 mg.) (from aqueous methanol), m. p. 78—80°. If kept slightly above the m. p. this solidified and then had m. p. 109—110°. The same compound was obtained when the dihydro-oxide (XXIII) (35 mg.) in acetic anhydride (2·5 ml.) and anhydrous sodium acetate (100 mg.) were heated under reflux for 1 hr. After crystallisation it had either m. p. 109—110° (blades) or m. p. 78—80° and then 109—110° (see above) (needles), $[\alpha]_D$ +168° (*c* 0·158) (Found: C, 81·85; H, 11·8. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Reduction of this *epi*-dihydro-oxide (XXV) (10 mg.) with sodium and ethanol as above gave the alcohol (XXVI) reported above (m. p. and mixed m. p.). Oxidation of this alcohol (11 mg.) in benzene–acetic acid (4 : 1; 5 ml.) with Kiliani chromic acid mixture (0·1 ml.) at room temperature with shaking for 15 min. gave back the *epi*-dihydro-oxide (XXV) in the two characteristic crystalline forms (m. p. and mixed m. p.).

Conversion of the Chloride (XIX) *into the Dienone* (XXII).—The chloride (XIX) (1·25 g.) in acetic acid (100 ml.) was refluxed for 2 hr. (evolution of hydrogen chloride). Addition of water and working up in the usual way gave the *dienone* (XXII) as felted needles (from aqueous methanol) (1·02 g.), m. p. 127—128°, $[\alpha]_D$ +99° (*c* 1·29), $\lambda_{max.}$ 271 mμ (ε 12,600), $\nu_{max.}$ 1728 (OAc), 1679 (conjugated ketone) and 1648 and 1618 (C=C) cm.$^{-1}$ (Found: C, 79·8; H, 10·5. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·45%). When this dienone (XXII) (140 mg.) in ethanol (15 ml.) containing potassium hydroxide (150 mg.) was heated to the b. p. under oxygen-free nitrogen it gave the known oxide (XXI) (82 mg.), identified by m. p., mixed m. p., rotation {$[\alpha]_D$ +89° (*c* 1·39; *l* = 0·5)}, and ultraviolet absorption spectrum.

The dienone (115 mg.) in dry ether (7 ml.) was treated with osmium tetroxide (100 mg.)

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in dry pyridine (3 ml.) in the dark at room temperature for 5 days. Working up by the hydrogen sulphide method [18] and chromatography of the product over alumina (Grade V) gave, on elution with ether–light petroleum mixtures, the *diol* (XX). Recrystallised from aqueous methanol this formed needles, m. p. 132—134°, $[\alpha]_D$ +210° (*c* 1·00; *l* = 0·5), $\lambda_{max.}$ 254 mμ (ε 9500), $\nu_{max.}$ 3484 and 3333 (OH), 1748 (OAc), 1678 and 1608 (cyclopentenone) cm.$^{-1}$ (Found: C, 74·0; H, 10·15. $C_{32}H_{52}O_5$ requires C, 74·35; H, 10·15%). This diol was recovered unchanged after attempted acetylation with pyridine–acetic anhydride at room temperature.

The dienone (320 mg.) in peracetic acid solution (0·084 active oxygen per ml.; 25 ml.) was left at 5° in the dark for 5 days. The white crystals that separated were filtered off. Recrystallisation from acetone–methanol gave the *hydroxy-oxide* (XXIV) (271 mg.) as needles, m. p. 223—224°, $[\alpha]_D$ +111° (*c* 0·63), $\lambda_{max.}$ 254 mμ (ε 7500), $\nu_{max.}$ 3425 (OH), 1686 and 1631 (cyclopentenone) cm.$^{-1}$ (Found: C, 79·0; H, 10·45. $C_{30}H_{46}O_3$ requires C, 78·9; H, 10·5%). This compound was recovered unchanged after treatment with pyridine–acetic anhydride for 16 hr. at room temperature or 2 hr. at 100°. It resisted oxidation with Kiliani chromic acid mixture. Reduction was effected by the following method. Liquid ammonia (at the b. p.) was saturated with excess of lithium (50—80 mg.; 10 minutes' stirring). The hydroxy-oxide (100 mg.) in dry tetrahydrofuran (15 ml.) was added (5 min.) and stirring continued (10 min.). Ammonium chloride (5 g.) was then added and the mixture was worked up in the usual way to give, after crystallisation from methanol, the dihydro-oxide (XXIII) (10 mg.), identified by m. p., mixed m. p., rotation, and infrared spectrum.

Toluene-p-sulphonyl and Methanesulphonyl Derivatives.—These were prepared in the following way. The alcohol (1 g.; or proportionate part) in pyridine (15 ml.) was treated with recrystallised toluene-*p*-sulphonyl chloride (2 g.) or redistilled methanesulphonyl chloride (1 ml.) at room temperature for 13 hr. The mixture was diluted with water and worked up in the usual way, all evaporations being conducted at room temperature (or lower) *in vacuo*. The *toluene-p-sulphonate* of 3β-hydroxylanost-8-en-7-one, crystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 188° (decomp.), $[\alpha]_D$ +12° (*c* 0·99), $\lambda_{max.}$ 228 and 254 mμ (ε 11,800 and 8400 respectively) (Found: C, 74·15; H, 9·5; S, 5·4. $C_{37}H_{56}O_4S$ requires C, 74·45; H, 9·45; S, 5·5%). The corresponding *methanesulphonate*, from the same solvent mixture, had m. p. 178—179° (decomp.), $[\alpha]_D$ +16° (*c* 1·01), $\lambda_{max.}$ 254 mμ (ε 8200) (Found: C, 71·7; H, 9·85; S, 6·1. $C_{31}H_{52}O_4S$ requires C, 71·5; H, 10·0; S, 6·15%). 3β-*Toluene*-p-*sulphonyloxylanosta-5,8-dien-7-one* crystallised from chloroform–methanol as rods, m. p. 167—168° (decomp.), $[\alpha]_D$ +10° (*c* 0·94), $\lambda_{max.}$ 228 and 248 mμ (ε 14,600 and 11,100 respectively) (Found: C, 74·8; H, 9·15. $C_{37}H_{54}O_4S$ requires C, 74·7; H, 9·15%). The corresponding *methanesulphonate*, crystallised from light petroleum, had m. p. 151—153° (decomp.), $[\alpha]_D$ +14° (*c* 0·98), $\lambda_{max.}$ 248 mμ (ε 10,100) (Found: C, 71·3; H, 9·5; S, 6·05. $C_{31}H_{50}O_4S$ requires C, 71·75; H, 9·7; S, 6·15%). The alcohol (IV; R = H) gave a *methanesulphonate* which crystallised from light petroleum as needles, m. p. 111—112° (decomp.), $[\alpha]_D$ +177° (*c* 0·83), $\lambda_{max.}$ 234 and 279 mμ (ε 5600 and 3100 respectively) (Found: C, 71·45; H, 9·65; S, 6·0. $C_{31}H_{50}O_4S$ requires C, 71·75; H, 9·7; S, 6·15%).

Preparation of the Model Umbellulone (XXX).—Tetrahydrophotodehydroergosteryl acetate [10] (1·0 g.) in dry pyridine (15 ml.) was added to a slurry of chromium trioxide (1·3 g.) in dry pyridine (25 ml.) and shaken in the dark under oxygen-free nitrogen for 6 days at room temperature. Dilution with water and working up in the usual way gave a product (1·0 g.) which, with methanol, afforded unchanged starting material (485 mg.). The mother-liquors were evaporated to dryness *in vacuo* and the residue was chromatographed over alumina (Grade V; 15 g.). Elution with benzene–light petroleum (1 : 19) and crystallisation from methanol gave the desired *umbellulone* (XXX) (60 mg.) as needles, m. p. 160—162°, $[\alpha]_D$ +112° (*c* 0·302), $\lambda_{max.}$ 232 and 278 mμ (ε 5200 and 3100 respectively), $\nu_{max.}$ 1721 (OAc) and 1667 and 1621 (umbellulone) cm.$^{-1}$ (Found: C, 79·65; H, 10·4. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%).

We thank Dr. E. L. Wheeler for the preliminary experiment indicated. One of us (M. R.) acknowledges with gratitude the award of a Research Assistantship (Chelsea College of Science and Technology).

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[*Received, July 18th,* 1960.]

[18] Barton and Elad, *J.*, 1956, 2085.

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239. *Absorption Spectra of Ketones. Part VI.*† *Intramolecular Charge-transfer Spectra, and Further Examples of Intensified* $n \longrightarrow \pi^*$ *Transitions.*

By H. Birnbaum, R. C. Cookson, and N. Lewin.

The ultraviolet spectra of several benzo-homologues of bicyclo[2,2,2]octenone show that progressive reduction in the ionisation potential of the aromatic ring increases the intensity of the $n \longrightarrow \pi^*$ band of the ketone. The long-wavelength bands of α-diketones are affected in the same way. The α-diketone group is a good acceptor for intramolecular charge-transfer, and absorption apparently due to such transitions is shown where the donor is a double bond (VI) or two benzene rings (VII).

During the last few years, in seeking a suitable framework for systematic study of intramolecular charge-transfer spectra and the effects of perturbation on $n \longrightarrow \pi^*$ transitions,[1,2,3] we have made a variety of bicyclo[2,2,2]octanes with electron-donors (tetrasubstituted double bonds or aromatic rings) in one bridge and acceptors (carbonyl, diketone, or quinone groups) in another. This paper reports some of the more interesting spectra.

The increase in intensity of the $n \longrightarrow \pi^*$ band produced by supply of electrons to the phenyl group in non-planar α-phenyl ketones [1] is illustrated by the spectra (Table 1) of

Table 1. *Absorption maxima* (mμ) (ε *in parentheses*).

No.	Compound		Solvent
1	(I; R = R′ = Ac)	264 (480), 300 (310), 307 (310)	EtOH
2	(I; R = Me, R′ = H)	281 (1700), 309 (720)	EtOH
3	(I; R = R′ = H)	284 (2150), 309 (760)	EtOH
4	(II)	240—242 [a] (4000), 283 (2100), 311 (800)	EtOH
5	(I; R = R′ = H)	271 (7000), *ca.* 300 [a] (4300), 317—329 (3200)	0·1N-NaOEt–EtOH
6	(III)	238 (5000), 430—435 (130)	Dioxan
7	(IV; R = Ac)	252 (4100), 279 (3500), 438 (170)	Dioxan
8	(IV; R = H)	270 (7100), 299—304 [a] (2400), 446 (760)	EtOH
9	(IV; R = H)	258—266 [a] (6700), 450 (920)	0·1N-NaOEt–EtOH
10	(V) [c]	293 (15), 478,[b] 465,[b] 457,[b] 447 [b]	Cyclohexane
11	(VI)	238 (2600), 271 (1750), 460 (150)	Cyclohexane

[a] Inflexion. [b] ε 30—40. [c] Alder, Schäfer, Esser, Krieger, and Reubke, *Annalen*, 1955, **593**, 23.

the ketones (I) and (II) obtainable from the dimer [4] of 2-acetoxy-2-methylcyclohexadienone. Changing the substituent in the benzene ring *para* to the CO group from OAc to OH (or OMe) to O^- causes a sharp increase in the intensity of the band at about 310 mμ, but hardly affects its position. For the spectra in neutral ethanol (Nos. 1—4) the tail of the absorption at shorter wavelengths contributes negligible intensity at 310 mμ; extrapolation suggests that in alkaline solution (No. 5) up to half the intensity of the longest-wavelength band may come from the tail of the shorter band, which is also responsible for at least some of the apparent shift in the $n \longrightarrow \pi^*$ band to longer wavelength. This increase in intensity without change in energy is consistent with all the long-wavelength bands' being $n \longrightarrow \pi^*$ transitions.[1,3]

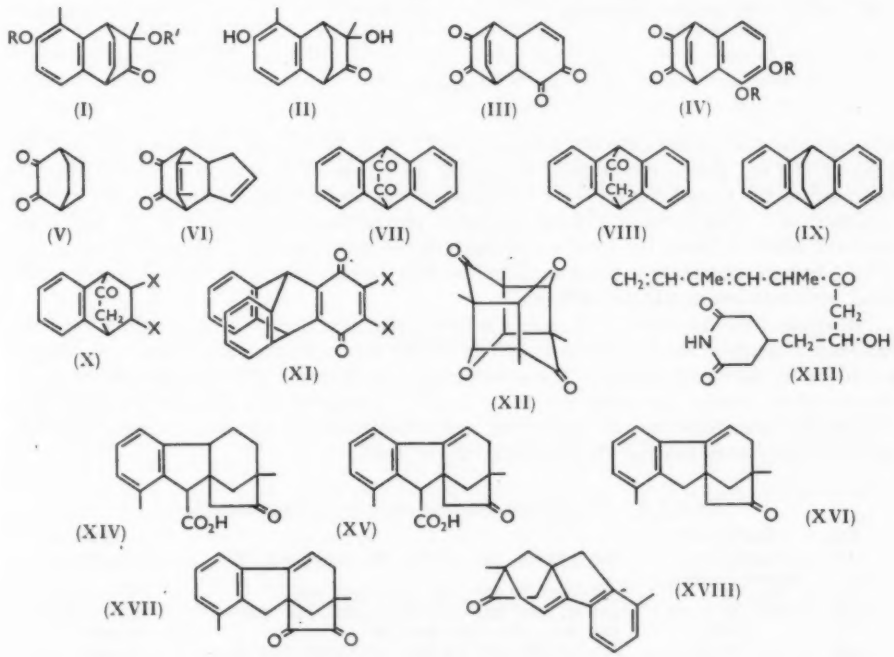
Similar compounds containing an α-diketone group were obtained from the dimer [5,6] (III) of *o*-benzoquinone, and again the intensity of the band at longest wavelength increases in the order: OAc > OH > O^- (Nos. 6—9). [The band centred on 450 mμ in alkali

† Part V, *J.*, 1956, 3675.

[1] Cookson and Wariyar, *J.*, 1956, 2302.
[2] Cookson and Lewin, *Chem. and Ind.*, 1956, 984.
[3] Labhart and Wagnière, *Helv. Chim. Acta*, 1959, **42**, 2219.
[4] Metlesics and Wessely, *Monatsh.*, 1957, **88**, 108.
[5] Patchett and Witkop, *J. Org. Chem.*, 1957, **22**, 1477.
[6] Harley-Mason and Laird, *J.*, 1958, 1718.

(No. 9) is very broad, so that, if it is due to the α-diketone perturbed by the catechol anion, the ε value underestimates its relative strength. The dimer (III) and especially its enol (IV; R = H) were unstable in solution.] All these compounds show great intensification of the longest-wavelength band compared with the parent bicyclo[2,2,2]octanedione [7] (V) (No. 10).

The strong absorption (No. 8) of the compound (IV; R = H) at 270 mμ, where catechol has ε about 2500, and at shorter wavelengths is remarkable. While much of the strength of the 270 mμ band might have come from intensification of the forbidden *B*-band of benzene, it was tempting to consider that a contribution might come from separate charge-transfer from the catechol group (of low ionisation potential) to the α-diketone group (of high electron-affinity). The diketone [8] (VI) was therefore particularly interesting, because



the absorption of the isolated chromophores it contains is so weak. In fact it did show (No. 11) a fairly strong band at 238 mμ, assigned to the charge-transfer transition.† The next step was to put a benzene ring on each side of the α-diketone: the spectrum of the appropriate compound (VII) showed in a spectacular degree all the effects that have been mentioned.

The monoketone (VIII) (No. 13; Table 2) showed an intense $n \longrightarrow \pi^*$ band, about twice as strong as that of the analogous ketones [1] with only one benzene ring (X). In ethanol the fine structure of the $n \longrightarrow \pi^*$ band evident in hexane was not resolved: it appeared as a broad band with a maximum at 296 mμ (ε 730) and a shoulder at 302—306 mμ (ε 675), the expected slight shift to shorter wavelength. The spectrum of the oxime followed that of the ketone (VIII) very closely, but the $n \longrightarrow \pi^*$ band was, of course,

† We are most grateful to Professor L. Horner for his kindness in providing a sample of compound (VI).

[7] Alder, Schäfer, Esser, Krieger, and Reubke, *Annalen*, 1955, **593**, 23.
[8] Horner and Spietschka, *Annalen*, 1953, **579**, 159.

missing. Mutual perturbation of the transitions of both the α-diketone and the benzene chromophores, and the superposition of an extraordinarily intense charge-transfer band make the spectrum (No. 14) of the diketone (VII) dramatically different from the sum of the spectra of the two isolated systems present in the diketone (V) (No. 10) and the dihydroanthracene (IX) (No. 12). The longest-wavelength band of the α-diketone is even more

TABLE 2. *Absorption bands* (mμ) (ε *in parentheses*).

No.	Compound	Charge-transfer band	Benzene band	Carbonyl band	Diketone band	Solvent
12	(IX)	—	253 [a] (500), 259 [a] (745), 265 (1350), 272 (1770)	—	—	Cyclohexane
13	(VIII)	—	253 (820), 261 [a] (740), 266·5 (975), 273·5 (970)	287 (530), 296·5 (710), 307·5 (735), 319 (442)	—	Hexane
14	(VII)	245 (28,000) 253 (46,000)	272 (3430)	290 (2890)	339 (210), 357 (270), 377 (420), 458 (980)	Cyclohexane

[a] Inflexion.

intense than that of the catechol derivative (IV; R = H) (No. 8), and the band with its peak at 290 mμ also is remarkably strong for an $n \longrightarrow \pi^*$ transition. [Unlike the 300 mμ band of the monoketone (VIII) this band shows no detectable fine structure even in cyclohexane]. The band at 272 mμ probably represents enhancement of the forbidden aromatic band at about the same wavelength in the monoketone (VIII) and hydrocarbon (IX). But the spectrum is dominated by the very intense intramolecular charge-transfer band with maxima at 246 and 253 mμ.†

In ethanol the diketone (VII) gave a solution that was only very pale yellow, and the spectrum resembled that of the monoketone (VIII), no doubt through addition of ethanol to one of the carbonyl groups. The structure of the diketone (VII), important to prove because of its unusual spectrum, was confirmed [9] by formation of a quinoxaline, hydrolysis to 9,10-dihydroanthracene and oxalic acid, and conversion with alkaline hydrogen peroxide into 9,10-dihydroanthracene-*cis*-9,10-dicarboxylic acid.

TABLE 3. *Absorption maxima* (mμ) (ε *in parentheses*).

No.	Compound		Solvent
15	2,3-Dimethylbenzoquinone [b]	250 (18,000), 257 (16,000), 337 (1100), 425 (35)	Chloroform
16	(XI; X = H)	243—247 (20,000), 300 (820), 415 (320)	Chloroform
17	(XI; X = Cl)	275 (17,000), 321—322 (950), 433—434 (250)	Chloroform
18	(XIV) [c]	265 (360), 274 (300), 300 (31)	Ethanol
19	(XV) [c]	260 (14,000), 269 (12,000), 290 (3200), 300 (2750)	Ethanol
20	(XVI) [c]	259·5 (13,000), 269 (12,000), 290 (4200), 301·5 (4200)	Ethanol
21	(XVII) [c]	*ca.* 250 (14,000), 257 (16,000), 267 (13,000), 290 (4500), 301 (4500)	Ethanol

[a] Inflection. [b] Flaig and Salfeld, *Annalen*, 1958, **618**, 117. [c] Cross, Grove, MacMillan, and Mulholland, *J.*, 1958, 2520.

Quinones are good acceptors in intermolecular charge-transfer (where the donor and acceptor in the complex presumably occupy parallel planes) so that it is interesting that the quinones [10,11] (XI; X = H or Cl) (Nos. 16—17; Table 3) gave no clear evidence of intramolecular charge-transfer, although the intensity of the longest-wavelength band was

† The spectrum of the α-methylene derivative of the ketone (VIII) (*i.e.* VII, with one :O replaced by :CH_2), which has just been reported (Snyder and Clement, *J. Amer. Chem. Soc.*, 1960, **82**, 1424), also shows strong interaction: $\lambda_{max.}$ 247[a] (5400), 274[a] (3200), 285 (3800) and 343 mμ (730).

[9] Cf. Vaughan and Yoshimine, *J. Org. Chem.*, 1957, **22**, 528.
[10] Clar, *Ber.*, 1931, **64**, 1676.
[11] Bartlett, Ryan, and Cohen, *J. Amer. Chem. Soc.*, 1942, **64**, 2649.

again enhanced compared with those for simple quinones [12] (*e.g.* No. 15). One obvious difference between the dihydroanthracenes with α-diketone (VII) and *p*-quinone (XI) as acceptor groups is the less favourable orientation of the transition moment of the latter.

Yates and Jorgenson [13] recently reported that the photodimer (XII) of 2,6-dimethyl-4-pyrone shows an unusual spectrum for a compound saturated but for the carbonyl groups: presumably the maximum at 233 mμ (ε 6600) arises from charge-transfer from the oxygen atoms to the carbonyl groups.

The spectrum of streptimidone [14] (XIII) clearly shows the effect of lowering the ionisation potential of the double bond in heightening the intensity of the $n \longrightarrow \pi^*$ transition of βγ-unsaturated ketones. Where acetone has ε 16 and analogous βγ-unsaturated ketones [1] have ε up to 300, streptimidone has a maximum at 291 mμ (ε 790). What seem to be even more extreme examples of the same effect are provided by the γδ-unsaturated ketone, dehydrogibberic acid (XV) and its derivatives.[15] If the maxima at 290 and 300 mμ (No. 19—21) really do come from the $n \longrightarrow \pi^*$ transition of the carbonyl perturbed by the styrene group, they represent the most intense carbonyl absorption yet recorded. Labhart and Wagnière [3] have attributed the increased strength of the $n \longrightarrow \pi^*$ transitions of βγ-unsaturated ketones to the overlap of the *p*-orbital of the oxygen atom with the π-orbital of the double bond in the ground state, which happens to have nearly the same energy. A model (XVIII) of " gebberone " (XVI) shows that the overlap of these orbitals, even allowing for the lower ionisation potential of the styrene double bond, can be only slight. The intensity here may come from the charge-transfer transition, which should have about the same energy.

Experimental

Ultraviolet spectra were measured on a Unicam S.P. 500 spectrometer and positions of maxima were determined graphically.

The diacetate (I; R = R′ = Ac) was made by boiling the dimer of 2-methylquinol diacetate with sodium acetate in acetic anhydride according to Wessely's directions.[4] After recrystallisation from ether it had m. p. 158°. The diol (I; R = R′ = H), crystallised from ethyl acetate, had m. p. 181°. The monomethyl ether (I; R = Me; R′ = H) (from methanol) had m. p. 151°. The dihydro-compound (II) (from methanol) had m. p. 183—184°.

The dimer (III) of *o*-benzoquinone, made by oxidation of catechol with silver oxide in acetone [6] in the dark, formed yellow crystals, double m. p. 125—130°, then 194—195°. The enolic tautomer (IV; R = H) crystallised from ethyl acetate–light petroleum (b. p. 40—60°) in orange-yellow plates, m. p. 193—194°, and the diacetate (IV; R = Ac) separated from the same solvent in yellow crystals, m. p. 141—142°.

9,10-Dihydro-11-oxo-9,10-ethanoanthracene [9,16] (VIII), got by oxidation of the alcohol with chromic oxide in pyridine, or cyclohexanone and aluminium t-butoxide in toluene, or benzoquinone and aluminium t-butoxide in benzene, had m. p. 152—153° after crystallisation from alcohol or light petroleum (b. p. 60—80°).

The monoketone (VIII) was oxidised with an equal weight of selenium dioxide in boiling acetic acid for 6 days or in dioxan at 165° for 2 hr. Recrystallisation from benzene or ethyl acetate yielded the yellow diketone (VII), m. p. 202—203° (Found: C, 82·0; H, 4·3. Calc. for $C_{16}H_{10}O_2$: C, 82·05; H, 4·4%).

The hydrazone of the monoketone (VIII) with sodium ethoxide in ethanol at 160° for 20 hr. formed the hydrocarbon (IX), m. p. 145—146° (from water–methanol).

Oxidation of dihydroxytriptycene with potassium bromate in acetic acid [11] gave the quinone (XI; X = H), m. p. 304° (from acetic acid). The dichloro-derivative [10] (XI; X = Cl) was made directly from the adduct of anthracene and benzoquinone by passing chlorine through

[12] Flaig and Salfeld, *Annalen*, 1958, **618**, 117.
[13] Yates and Jorgenson, *J. Amer. Chem. Soc.*, 1958, **80**, 6150.
[14] van Tamelen and Haarstad, *J. Amer. Chem. Soc.*, 1960, **82**, 2974.
[15] Cross, Grove, MacMillan, and Mulholland, *J.*, 1958, 2520.
[16] Noland, Baker, and Freeman, *J. Amer. Chem. Soc.*, 1956, **78**, 2233.

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a solution in boiling acetic acid. After crystallisation from acetic acid the dichloroquinone had m. p. 291° (decomp.).

We are indebted to the Royal Society, Imperial Chemical Industries Limited, and the U.S. Air Force (European Office, Brussels) for grants, and to Dr. J. Hudec for valuable discussions.

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240. *Some Reactions of the Dimethylamino Radical,* $\cdot NMe_2$.

By B. R. COWLEY and WILLIAM A. WATERS.

The radical $\cdot NMe_2$ has been obtained by pyrolysis of tetramethyltetrazen in a number of organic liquids. Some evidence of dehydrogenation of non-1-ene, cyclohexanol, and benzyl alcohol has been obtained, but there was no indication of nuclear substitution of naphthalene or anthracene. The $\cdot NMe_2$ radical combines with α-methylstyrene (isopropenylbenzene) to give a number of bases derived from the radicals $Me_2N{\cdot}CH_2{\cdot}CPhMe\cdot$ and $Me_2N{\cdot}CH_2{\cdot}CPhMe{\cdot}CH_2{\cdot}CPhMe\cdot$ by addition or disproportionation.

JUST as alkyl radicals can be formed by the pyrolysis of aliphatic azo-compounds, the dimethylamino radical can be obtained by the pyrolysis of tetramethyltetrazen:[1]

$$Me_2N{\cdot}N{:}N{\cdot}NMe_2 \longrightarrow N_2 + 2Me_2N\cdot$$

These radicals interact both by combination and by disproportionation, for the identified products of this pyrolysis, in the vapour phase,[2] are nitrogen, tetramethylhydrazine, dimethylamine, and a polymer of the Schiff's base, $CH_2{:}NMe$. From the few figures published, about as many radicals appear to interact by disproportionation as by combination.

Liquid-phase reactions of dimethylamino radicals have as yet been examined only by Erusalimsky, Dolgoplosk, and Kavunenko,[3] who have shown that these radicals can dehydrogenate cumene, forming dimethylamino (92%) and dicumyl (44%), and that they evidently combine with α-methylstyrene (isopropenylbenzene). No dimethylamine was generated from a dilute solution in the latter solvent, but the basic products were not examined.

$$Me_2N\cdot + Ph{\cdot}CHMe_2 \longrightarrow Me_2NH + Ph{\cdot}CMe_2\cdot$$
$$2Ph{\cdot}CMe_2\cdot \longrightarrow Ph{\cdot}CMe_2{\cdot}CMe_2Ph$$

We have now investigated the products of pyrolysis of tetramethyltetrazen in a number of organic liquids. From solutions in molten naphthalene, and in anisole containing anthracene, 62% of dimethylamine was involved but production of aromatic tertiary amines could not be detected. This appears to indicate that $\cdot NMe_2$ is less reactive than $\cdot NH_2$.[4] Decomposition of the tetrazen in a 5% solution in non-1-ene yielded 72% of dimethylamine and a high-boiling hydrocarbon mixture which appeared to contain both terminal ($\cdot CH{:}CH_2$) and *trans*-non-terminal ($\cdot CH{:}CH\cdot$) double bonds, but there was very little other basic material. Thus some allylic dehydrogenation seems to have occurred:

$$Me_2N\cdot + R{\cdot}CH_2{\cdot}CH{=}CH_2 \longrightarrow Me_2NH + R{\cdot}\overset{\cdot}{C}H{\cdot}CH{:}CH_2$$

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[1] Rice and Grelecki, *J. Amer. Chem. Soc.*, 1957, **79**, 2679.
[2] Watson, *J.*, 1956, 3677; Watson and Waring, *Canad. J. Chem.*, 1960, **38**, 298.
[3] Erusalimsky, Dolgoplosk, and Kavunenko, *Zhur. obshchei Khim.*, 1957, **27**, 267.
[4] Seaman, Taylor, and Waters, *J.*, 1954, 4690; Albisetti, Coffmann, Hoover, Jenner, and Mochel, *J. Amer. Chem. Soc.*, 1959, **81**, 1489.

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Decompositions in cyclohexanol, cyclohexanone, and benzyl alcohol gave 60—70% yields of dimethylamine, which again indicate that $\cdot NMe_2$ can effect some dehydrogenation of these liquids. Though reactions between amines and carbonyl compounds obscure the picture, yet, from the decomposition in benzyl alcohol, benzaldehyde has been isolated together with much smaller amounts of hydrobenzoin, benzil, benzyl benzoate, and a base which has proved to be *NN'*-dimethyl-1,2-diphenylethylenediamine, $(\cdot CHPh\cdot NHMe)_2$. Some of these minor products may have been formed from benzaldehyde, the reactions of which with dimethylamino radicals are very complex and will be reported later.

Products of the decomposition of tetramethyltetrazen in α-methylstyrene have been separated by distillation and chromatography and have been examined. From much more concentrated solutions than that used by Erusalimsky *et al.*, 12—26% of dimethylamine was evolved and 42—45% of the dimethylamino radicals could be accounted for as addition products of the α-methylstyrene. There was also formed a little 2,5-diphenylhex-1-ene and some hydrocarbon polymer. From the basic product a 15—20% yield of 3-dimethylamino-2-phenylpropene (II) was isolated and identified by reduction and methylation to give trimethyl-2-phenylpropylammonium iodide. Clearly, the base (II) has been formed by the following reactions:

$$Ph\cdot CMe{:}CH_2 + \cdot NMe_2 \longrightarrow \cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (I)}$$
$$\cdot CMePh\cdot CH_2\cdot NMe_2 + \cdot R \longrightarrow CH_2{:}CPh\cdot CH_2\cdot NMe_2 \text{ (II)} + RH$$

in which a dimethylamino-radical has added, as would be expected, to the CH_2 group of the olefin to give radical (I).

A similar amount of the reaction product consisted of a mixture of related tertiary bases $C_{20}H_{25}N$ and $C_{20}H_{27}N$, probably 5-dimethylamino-4-methyl-2,4-diphenylpent-2-ene (IV) and 1-dimethylamino-2-methyl-2,4-diphenylpentane (V), whilst 3% consisted of a solid, $C_{22}H_{32}N_2$, possibly 1,4-bisdimethylamino-2,3-dimethyl-2,3-diphenylbutane (VI). These are the expected products of the following radical reactions, analogues of which, on use of trichloromethyl radicals, have been elucidated by Kharasch, Simon, and Nudenberg: [5]

$$\text{(I) } \cdot CMePh\cdot CH_2\cdot NMe_2 + CMePh{:}CH_2 \longrightarrow \cdot CMePh\cdot CH_2\cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (III)}$$
$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$
$$\text{(VI) } (CMePh\cdot CH_2\cdot NMe_2)_2 \qquad CMePh{:}CH\cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (IV)}$$
$$+ CHMePh\cdot CH_2\cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (V)}$$

Experimental

Tetramethyltetrazen was prepared by oxidizing *NN*-dimethylhydrazine (Eastman Kodak " Practical " material) with mercuric oxide [6] (yield 50%). It was redistilled from fused barium oxide and stored at 0° (b. p. 33—34°/15 mm.).

Decomposition in Non-1-ene.—The hydrocarbon (Shell Chemicals Co.), when freed from inhibitor, dried, and distilled from a little picric acid, had b. p. 37—38°/13 mm. A mixture of the tetrazen (3·5 g., 0·03 mole) and non-1-ene (64 g., ~0·5 mole) was refluxed for 44 hr. at 145—150° in a stream of dry, oxygen-free nitrogen. The issuing gases were passed through N-hydrochloric acid; titration, to Methyl Red, showed that 0·046 equiv. (77% of the $\cdot NMe_2$ groups) of base had been evolved. The acid solution was evaporated to dryness, the residue, covered with benzene (30 ml.), was basified with sodium hydroxide, and the benzene layer was dried. Addition to it of a saturated solution of picric acid in benzene gave yellow crystals, m. p. 154—156°, which after one recrystallisation did not depress the m. p. (158°) of dimethylamine picrate. The liquid product was extracted with water and then dilute acid but this procedure removed only 0·1 g. of brown, unsaturated, basic material. Non-1-ene was removed from the acid-washed liquid by distillation at 15 mm. and the remainder (12 g.) was chromatographed through alumina by use of light petroleum (b. p. 60—80°) and then fractionated at

[5] Kharasch, Simon, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 328.
[6] Bull, Seaton, and Audrieth, *J. Amer. Chem. Soc.*, 1958, **80**, 2516.

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1·5 mm. into colourless oils: (*a*) 4 g., b. p. 142—180°, having strong infrared absorptions of almost equal intensity at 915 and 965 cm.$^{-1}$; (*b*) 3 g., b. p. 180—250°; (*c*) 2 g., b. p. >250°, having weaker absorptions at these frequencies. The absorption spectra of those oils indicated that they were mixtures of dimeric and polymeric unsaturated hydrocarbons.

Decomposition in boiling cyclohexanol (80 g.) was carried out similarly by using 4·64 g. of the tetrazen. 0·052 Equiv. (68%) of dimethylamine was liberated, but acid-extraction of the residue gave only a small amount of dark basic material. The neutral remainder contained ketonic material (<0·3 g.; absorption at 1700 cm.$^{-1}$) but the presence of cyclohexanone could not be established. A similar decomposition in cyclohexanone gave 76% of dimethylamine and yielded a deep brown liquid which, on acidification, deposited a black tar insoluble in ether. No identifiable products could be separated from the neutral remainder.

The decomposition at 145—150° of the tetrazen (11·6 g.) in molten naphthalene (51 g.) gave 0·124 equiv. (62%) of volatile base. Some basic tar was formed, but this gave only a few drops of a dark oil soluble in ether. The tetrazen (4·4 g.) and anthracene (6·7 g.) were refluxed at *ca.* 153° for 2 days in anisole (100 ml.) under nitrogen; 0·047 equiv. (62%) of dimethylamine was evolved. After removal of the anisole, extraction of the remainder gave 0·25 g. of basic tar, and 5 g. of anthracene were recovered.

Decomposition in Benzyl Alcohol.—A mixture of the tetrazen (11·6 g.) and benzyl alcohol (95 g.; b. p. 96—97°/15 mm.; purified by distillation from 2,4-dinitrophenylhydrazine) was heated at 145—150° for 43 hr. under nitrogen; 0·132 equiv. (66%) of volatile bases was evolved. The residual liquid was extracted with saturated aqueous sodium hydrogen sulphite. Decomposition of this extract with sodium carbonate followed by steam-distillation gave 2 ml. of an oil, consisting mainly of benzaldehyde [dinitrophenylhydrazone (4 g.), m. p. and mixed m. p. 234—237°].

The remaining product was distilled in steam to remove benzyl alcohol, and the residue, in ether, was extracted with 4N-hydrochloric acid. The remaining ether solution contained 8·1 g. of a green liquid which was dissolved in light petroleum and chromatographed on 5% deactivated alumina (500 g.). Light petroleum–benzene (9 : 1) eluted a yellow oil, A (0·64 g.), with $\nu_{max.}$ at 1715, 1265, and 1110 cm.$^{-1}$. Light petroleum–benzene (3 : 1) extracted 0·15 g. of an oil containing some crystals, B. Benzene eluted unchanged benzyl alcohol (2·8 g.), and ether–benzene eluted more benzyl alcohol (1·4 g.) together with yellow crystals, C (0·34 g.), with $\nu_{max.}$ at 3300, 1035, 1020, 758, and 700 cm.$^{-1}$.

Rechromatography of oil A gave a very pale yellow product (0·41 g.) with an infrared spectrum identical with that of benzyl benzoate. Hydrolysis of this with 25% aqueous potassium hydroxide gave benzoic acid (0·11 g.), m. p. and mixed m. p. 121°, and benzyl alcohol (3,5-dinitrobenzoate, m. p. and mixed m. p. 112°). Fraction B on rechromatography gave more benzyl benzoate together with benzil, m. p. and mixed m. p. 94—94·5°. Recrystallisation of the crystals C from ethanol gave colourless plates of hydrobenzoin, m. p. and mixed m. p. 135°. Basification of the acid extract gave a pale brown oil (4·15 g.) which, by chromatography through deactivated alumina, gave a little benzyl alcohol (1·12 g.), a yellow oil (1·09 g.), $\nu_{max.}$ 2750—2780m cm.$^{-1}$ (NMe), and a solid (0·48 g.) which, after crystallisation from acetone, gave prisms, m. p. 134° (Found: C, 80·0; H, 8·4; N, 11·6; NMe, 18·1%; *M*, 216. Calc. for $C_{16}H_{20}N_2$: C, 80·0; H, 8·4; N, 11·7%; *M*, 240), $\nu_{max.}$ (in Nujol) 3270, 2770, 1155, 1137, 1126, and 1105 cm.$^{-1}$. The infrared spectrum of the prisms in carbon tetrachloride solution had $\nu_{max.}$ at 3305 and 2805 cm.$^{-1}$, indicating the presence of a NHMe group.[7] The m. p. of this substance was not depressed on admixture with *NN'*-dimethyl-1,2-diphenylethylenediamine, prepared by Fischer and Römer's method,[8] and the two samples had coincident infrared spectra.

Decomposition in α-Methylstyrene.—The tetrazen (11·6 g.) and α-methylstyrene (75 g.; distilled from picric acid; b. p. 58°/16 mm.) were heated together at 145—150° for 2 days under purified nitrogen and gave 26% and 12% of dimethylamine in successive experiments. The mixture was extracted with 2N-hydrochloric acid, and the remaining neutral liquid was dried and distilled, to give a small residue (1·6 g.), b. p. 150—200°/8 mm., which, in light petroleum, was chromatographed through activated alumina. This yielded a colourless liquid (1·16 g.), n_D^{25} 1·5652, with absorptions at 1060, 895, 780, 765, and 700 cm.$^{-1}$, the absorption at 895 cm.$^{-1}$, typical of RR'C:CH_2, being relatively less intense than that of α-methylstyrene (Found: C, 91·6; H, 8·6. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%). These observations indicate

[7] Hill and Meakins, *J.*, 1958, 760.
[8] Fischer and Römer, *J. prakt. Chem.*, 1906, **73**, 441.

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that the liquid is 2,5-diphenylhex-1-ene, n_D^{25} 1·5621, which has been obtained by dimerising α-methylstyrene. Quantitative hydrogenation in glacial acetic acid over Adams catalyst indicated the presence of one double bond; the product absorbed only slightly at 895 cm.$^{-1}$.

The acid extract was basified and the organic bases (32 g.) were collected, dissolved in light petroleum, and chromatographed through 5% deactivated alumina. The successively eluted fractions were further separated by fractional distillation at reduced pressure. Three main products were obtained: X, b. p. 180—181°/11 mm., n_D^{25} 1·5486, $\nu_{max.}$ 2820, 2780, 1040, 1025, 900, 835, 780, 763, and 700 cm.$^{-1}$ (yields 19%, 25%) (Found: C, 85·0, 84·9; H, 9·4, 9·45; N, 5·4, 5·3%; *M*, 232. Calc. for $C_{20}H_{27}N$: C, 85·3; H, 9·7; N, 5·0%; *M*, 281); Y (more strongly adsorbed), b. p. 85°/8 mm., $\nu_{max.}$ 2820, 2780, 1035, 1020, 910, 855, 845, 780, 765, and 703 cm.$^{-1}$ (yields 20%, 16%) (Found: C, 81·8; H, 9·5; N, 8·5. $C_{11}H_{15}N$ requires C, 81·9; H, 9·4; N, 8·7%); and Z, which again slowly solidified, to give crystals, m. p. 100—101°, from light petroleum (b. p. 48—60°) (yield 3%) (Found: C, 81·9; H, 10·1; N, 7·9. $C_{22}H_{32}N_2$ requires C, 81·4; H, 9·9; N, 8·6%).

The liquid X gave a *picrate*, m. p. 152° (Found: C, 61·5; H, 5·7; N, 11·0. $C_{26}H_{30}N_4O_7$ requires C, 61·2; H, 5·9; N, 11·0%). Quantitative hydrogenation of X (from two different reactions) in glacial acetic acid over Adams catalyst indicated that 50% of X had one olefinic bond, the remainder being saturated. The hydrogenated product resembled X in all properties, except that its absorption at 900 cm.$^{-1}$ was very weak and it yielded the same picrate, m. p. 157°, as did untreated X. This evidence indicates that X is probably a 1 : 1 mixture of 5-dimethylamino-4-methyl-2,4-diphenylpent-2-ene and 1-dimethylamino-2-methyl-2,4-diphenylpentane, the picrate being that of the latter compound.

Liquid Y gave a *methiodide*, which formed cream-coloured crystals, m. p. 139°, from ethanol–ether (Found: C, 47·8; H, 5·9; N, 4·7; I, 41·3. $C_{12}H_{18}NI$ requires C, 47·5; H, 6·0; N, 4·6; I, 41·9%). Hydrogenation of Y indicated the presence of one olefinic bond: the product had very weak absorption at 910 cm.$^{-1}$ and gave a methiodide, m. p. 158—158·5°, corresponding in properties to trimethyl-2-phenylpropylammonium iodide [9] (Found: C, 47·2; H, 6·8; N, 4·6; I, 41·6. Calc. for $C_{12}H_{20}NI$: C, 47·2; H, 6·6; N, 4·6; I, 41·6%). This establishes that Y is *3-dimethylamino-2-phenylpropene*.

Material Z, from its analysis, polar character, and spectrum seems to be *1,4-bisdimethylamino-2,3-dimethyl-2,3-diphenylbutane*.

A synthesis of X was attempted; α-phenylpropionaldehyde was condensed with dimethylamine hydrochloride and paraformaldehyde in ethanol to give the Mannich base, *β-dimethylamino-α-methyl-α-phenylpropionaldehyde*, b. p. 118—124/9 mm., $\nu_{max.}$ 2830, 2780, 2730, 1730, 1040, 1030, and 865 cm.$^{-1}$ (Found: C, 75·8; H, 9·4; N, 6·8. $C_{12}H_{17}NO$ requires C, 75·4; H, 9·0; N, 7·3%), but attempts to condense this with the Grignard reagent of (1-bromoethyl)benzene failed, only 2,3-diphenylbutane,[10] m. p. 126°, being obtainable. A similar self-coupling of this Grignard reagent has been reported previously.[11]

One of us (B. R. C.) thanks the D.S.I.R. for a Research Studentship.

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[9] von Braun, Heider, and Neuman, *Ber.*, 1916, **49**, 2619.
[10] Heilbron and Bunbury, "Dictionary of Organic Compounds," II, Eyre and Spottiswoode, London, 1953, Vol. II, p. 273.
[11] Rupe and Tomi, *Ber.*, 1914, **47**, 3075.

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241. *The Ozonolysis of Polycyclic Hydrocarbons. Part II.*[1]

By P. G. Copeland, R. E. Dean, and D. McNeil.

The ozonolysis of phenanthrene, chrysene, picene, benzo[*g*]chrysene, dibenzo[*c*,*g*]phenanthrene, triphenylene, and benz[*a*]anthracene is described. In each case ozone attacks the bond(s) possessing the lowest bond-localisation energy. Improved preparations of these hydrocarbons are also reported.

The first paper [1] in this series described the ozonolysis of fluorene and benzo[*b*]fluorene and their ketones. This work is now extended to some non-linear polynuclear hydrocarbons, namely, phenanthrene, chrysene, picene, benzo[*g*]chrysene, dibenzo[*c*,*g*]phenanthrene, triphenylene, and benz[*a*]anthracene. Ozonolysis of phenanthrene and benz[*a*]anthracene, not of the others, has been reported previously.

The bond and the carbon localisation energies of these hydrocarbons have been calculated by Brown [2] and by Dewar [3] respectively. Except for benz[*a*]anthracene, the most reactive carbon atoms are at the ends of the most reactive bonds. It has now been found, by examination of the acids formed by oxidative decomposition of the ozonides, that scission of the molecule occurs at these bonds. Benz[*a*]anthracene is attacked also at the reactive 7 and 12 positions.

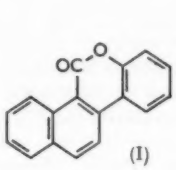
Our ozonolyses were carried out in inert solvents. Criegee [4] suggested that under these conditions the intermediate zwitterions react with themselves to form polymeric ozonides. Although, when freshly prepared, the ozonides of the hydrocarbons now examined contain active oxygen, liberating iodine from a solution of sodium iodide in acetic acid, they are not hydroperoxides as they give negative results in the lead tetra-acetate test. More precise characterization of the ozonides is difficult. Only that from phenanthrene has been examined previously, but it may be regarded as typical of the group, with the exception of benz[*a*]anthracene. Wibaut and de Boer [5] found the ozonide produced from phenanthrene in chloroform solution to have m. p. 136—138° and a molecular weight of 675 (cryoscopical in benzene). From this and elementary analysis, active-oxygen content, and infrared spectrum they concluded that it was trimeric. By repeated reprecipitation of phenanthrene ozonide formed under similar conditions Bailey and Mainthia [6] obtained a product, m. p. 139—140°, which they suggested was a higher polymer than that obtained by Wibaut and de Boer; they took the view that the ozonide of phenanthrene produced in chloroform solution is a mixture of polymers of varying chain lengths and that purification by precipitation merely concentrated one of these components. Our own experience confirms this view, the ozonide obtained by precipitation with light petroleum from chloroform solution having a similar melting point (131—132°) to that obtained by Wibaut and de Boer, but having a molecular weight of over 3000. The infrared spectrum of the ozonide shows a carbonyl band as well as bands at 9·5 and 9·6 μ corresponding to those observed by both the above workers. Since this study proved unproductive, the ozonides from the other hydrocarbons were decomposed immediately after formation.

Ozonolysis of some of the hydrocarbons in suspension in chloroform or carbon tetrachloride yielded substantial amounts of unchanged material. This difficulty was overcome by using *sym*-tetrachloroethane which is a satisfactory solvent for the ozonides and the hydrocarbons. Previous workers have established that in both reactive and inert solvents ozone attacks phenanthrene exclusively at the 9,10-bond, yielding diphenic acid on

[1] Part I, Copeland, Dean, and McNeil, *J.*, 1960, 3230.
[2] Brown, *J.*, 1950, 691, 3249.
[3] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.
[4] Criegee *et al.*, *Annalen*, 1949, **564**, 9; 1953, **583**, 12; *Chem. Ber.*, 1954, **87**, 766; 1955, **88**, 1878.
[5] Wibaut and de Boer, *Rec. Trav. chim.*, 1959, **78**, 183.
[6] Bailey and Mainthia, *J. Org. Chem.*, 1958, **23**, 1089.

oxidative decomposition of the resulting ozonide or peroxide.[5-8] Our experience has been that the decomposition with alkaline peroxide of the products of ozonolysis in an inert solvent of both phenanthrene and chrysene gives mainly alkali-insoluble resins and only small quantities of acidic materials. We obtained much higher yields of acids by oxidising the polymeric ozonides in 1 : 1 aqueous pyridine at 60—65° during 5—15 min. with powdered potassium permanganate. Phenanthrene thus gave an 81% yield of relatively much purer diphenic acid. Diphenic acid is probably formed by way of 2,2'-diformylbiphenyl since this was isolated (as its dioxime) (34%) on treating the ozonide with aqueous pyridine alone. Phenanthrene itself, with permanganate in pyridine under the same conditions, gave 51% yield of phenanthraquinone and <5% of diphenic acid. In an attempt to simplify the method by using pyridine as solvent for ozonolysis later decomposition with permanganate gave a slightly lower yield (74%) of less pure diphenic acid. In the present work, therefore, the hydrocarbons were ozonised in *sym*-tetrachloroethane, and the ozonides were then precipitated with light petroleum and oxidised without further purification by permanganate in pyridine solution.

Bond-order and localisation-energy calculations indicated that the equivalent 5,6- and 11,12-bonds of chrysene should be the most reactive. Cook and Schoental [9] found the 5,6-bond to be attacked by osmium tetroxide, which also catalyses the oxidation of chrysene by hydrogen peroxide to the 5,6-quinone. Ozone reacts at the same bond, giving a 48% yield of 2-*o*-carboxyphenyl-1-naphthoic acid. (None of this acid was formed when chrysene itself was treated with permanganate, 90% of the hydrocarbon being recovered unchanged whilst that converted gave a 65% yield of chrysene-5,6-quinone.) The same acid is formed by treatment of chrysene or its 5,6-quinone with hydrogen peroxide in acetic acid, together with a compound thought to be the lactone (I).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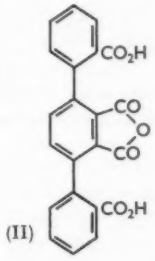
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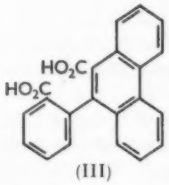
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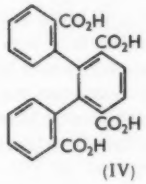
(IV)

Bond-localisation energies of picene indicate that the 5,6- and 7,8-bonds should be most susceptible to attack. In agreement, picene readily absorbed 2 mols. of ozone to give, on oxidative decomposition, a 35% yield of the anhydride (II). With an equimolar quantity of ozone there was only a 9% yield of the anhydride, 44% of the picene being recovered unchanged. It is concluded that initial attack yields picene 5,6-monozonide, the aromatic portion of which contains the phenylphenanthrene residue, and that since the 9,10-bond of phenanthrene is more reactive than the 5,6- and 7,8-bonds of picene further attack occurs preferentially at this bond to give the diozonide and thence the anhydride (II).

Benzo[*g*]chrysene with an equimolar quantity of ozone gave, by our method, a 69% yield of the acid (III), also in conformity with theoretical prediction.

The dibenzo[*c*,*g*]phenanthrene, like picene, contains two reactive bonds (1,2 and 7,8). These are simultaneously attacked by ozone, leading to the acid (IV) (65%).

Triphenylene is fairly resistant to oxidation, although fuming nitric acid,[10] or nitric

[7] O'Connor, Schmitt, and Moriconi, *Ind. Eng. Chem.*, 1957, **49**, 1701.
[8] Bailey, *J. Amer. Chem. Soc.*, 1956, **78**, 3811.
[9] Cook and Schoental, *J.*, 1950, 47.
[10] Mannich, *Ber.*, 1907, **4**, 160.

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acid followed by permanganate,[11] yields mellitic acid. Brown [2] is of the opinion that as it is so much less reactive than naphthalene it would not be expected to react with osmium tetroxide although it probably would do so with ozone at the 1,2-bond. The present work has confirmed this view. Like naphthalene it rapidly absorbs 2 mol. of ozone, to give 22% of phenanthrene-9,10-dicarboxylic anhydride; further reaction at the 9,10-bond of the residual phenanthrene nucleus is indicated by the formation of diphenic acid (8%). 3—4 Mols. of ozone give rise to large amounts of resin and minor quantities of diphenic acid.

The reactivity of benz[*a*]anthracene has been studied by several workers. Osmium tetroxide [12] and ethyl diazoacetate [13] attack the 5,6-bond, and oxidation to the 7,12-quinone occurs with chromic acid,[14] hydrogen peroxide in acetic acid,[15] or perbenzoic acid.[16] Cook and Schoental obtained the 7,12- and the 5,6-quinone together with small quantities of 3-*o*-carboxyphenyl-2-naphthoic and phthalic acid by oxidation with Milas reagent. This experimental evidence is in accord with the calculations by Brown [2] and Dewar [3] which indicate that the 5,6-bond has the least localisation energy, and the 7,12-positions the lowest *para*-localisation energy. Thus in this system the most reactive centres are not associated with the most reactive bonds. The ozonolysis of benz[*a*]-anthracene has been studied by Moriconi *et al.*[17] With equimolar amounts of ozone in methylene chloride or methanol or mixtures of the two, or in acetic acid, benz[*a*]anthracene-7,12-quinone was the main product, with small quantities of anthraquinone-1,2-dicarboxylic acid. Appreciable quantities of the starting material were recovered. When the benz[*a*]anthracene was treated with 3 and its 7,12-quinone with 2 mol. of ozone the same ozonide was formed and oxidative decomposition of this gave small yields of the anthraquinone diacid. Our method led to a similar amount of unchanged material (28%), 13% of the quinone, and 11% of 3-*o*-carboxyphenyl-2-naphthoic acid. The use of 2 mol. of ozone gave 17% of each of these products and no unchanged material. Benz[*a*]anthracene itself, with permanganate in aqueous pyridine, gave only an acidic resin, and 72% of the hydrocarbon was recovered. Similar treatment of the quinone gave 5% of anthraquinone-1,2-dicarboxylic acid, 77% of the quinone being unchanged. None of the acid was isolated on peroxide oxidation of the product from equimolar parts of ozone and benz[*a*]anthracene, the quinone (21·6%) and original material (31·6%) being the only compounds recovered.

The results of Moriconi *et al.*[17] suggest exclusive attack by ozone at the 7,12-positions whereas our additional isolation of the carboxyphenylnaphthoic acid confirms a measure of reactivity at the 5,6-bond. On the other hand, by our method of decomposition we were unable to detect any anthraquinone-1,2-dicarboxylic acid which they found. We consider that this acid arose by further attack of ozone on the 7,12-quinone formed during ozonolysis since reaction between this quinone and 2 mol. of ozone followed by treatment with alkaline peroxide gave the anthraquinone-1,2-diacid in 80% yield.

3-*o*-Carboxyphenyl-2-naphthoic acid (21%) and the quinone were produced also when benz[*a*]anthracene was treated with hydrogen peroxide in acetic acid; the quinone was the sole product obtained by Arnold and Larsen [15] using the same reagents under milder conditions.

Experimental

Apparatus.—This has been described previously.[1]

Ozonolysis of Phenanthrene.—Purified phenanthrene [18] (1·78 g., 10 mmoles) in carbon tetrachloride (60 ml.) was treated at −20° with an equimolar amount of ozone. The ozonide

[11] Juettner, *J. Amer. Chem. Soc.*, 1937, **59**, 1472.
[12] Badger, *J.*, 1949, 456.
[13] Badger, Cook and Gibb, *ibid.*, 1951, 3456.
[14] Graebe, *Annalen*, 1905, **340**, 257.
[15] Arnold and Larsen, *J. Org. Chem.*, 1940, **5**, 250.
[16] Roitt and Waters, *J.*, 1949, 3060.
[17] Moriconi, O'Connor, and Wallenberger, *J. Amer. Chem. Soc.*, 1959, **81**, 6466.
[18] Dornfeld, Callen, and Coleman, *Org. Synth.*, **28**, 19.

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(2·23 g.), precipitated by the addition of light petroleum (b. p. 40—60°; 300 ml.), was purified by repeated dissolution in chloroform and reprecipitation with light petroleum. The resulting white powder had m. p. 131—132° when freshly prepared (Found: C, 73·3; H, 4·8; active O,[19] 5·9, 5·8. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·5; active oxygen, 7·1%). After 3 weeks the ozonide had *M* 3100, 3200 (cryoscopically in benzene).

The crude ozonide (1·78 g.) in water (50 ml.) and redistilled pyridine (50 ml.) at 60—65° was treated portionwise with powdered potassium permanganate (6·5 g.) until the pink colour just persisted (5 min.). The mixture, after decolorisation with ethanol, was boiled, and filtered to remove manganese dioxide. The dioxide was washed with warm pyridine followed by 5% aqueous sodium carbonate. The filtrate and washings were then combined and the pyridine was removed by distillation. The alkaline solution was treated with charcoal and then acidified with 10% hydrochloric acid to give diphenic acid (1·90 g.), m. p. and mixed m. p. 230—231°, having the correct infrared absorption. The aqueous acid liquors were evaporated to dryness and the residue extracted with boiling acetone to give more diphenic acid (0·05 g., total yield 81%).

In another experiment the crude ozonide from phenanthrene (1·78 g.) was left for 12 hr. in water (50 ml.) and pyridine (50 ml.). Ether (100 ml.) was added to the solution and the pyridine removed with hydrochloric acid. The ethereal layer was washed, dried, and evaporated to give a yellow oil from which 2,2′-diformylbiphenyl was isolated as its dioxime (0·82 g., 34%), separating from aqueous ethanol as prisms, m. p. 180° (Bailey [8] gives m. p. 184—186°) (Found: C, 70·1; H, 5·2; N, 11·75. Calc. for $C_{14}H_{12}N_2O_2$: C, 70·0; H, 5·0; N, 11·7%).

Oxidation of phenanthrene (1·78 g.) by the above technique gave unchanged phenanthrene (0·6 g., 34%), phenanthraquinone (0·71 g., 51%), and diphenic acid (0·08 g., 5%).

With pyridine as solvent at 0° about 1·7 mol. of ozone were required for complete conversion, since the solvent was also attacked. Permanganate decomposition then yielded crude diphenic acid (74%), m. p. 222—224°.

Ozonolysis of phenanthrene (3·56 g., 20 mmoles) in *sym*-tetrachloroethane (60 ml.) at 0°, followed by treatment for 1 hr. at the same temperature with 30% hydrogen peroxide (15 ml.) and 10% aqueous sodium hydroxide (50 ml.), gave a yellow alkali-insoluble resin (2·82 g.) after removal of the solvent in steam. Acidification of the filtrate with 10% hydrochloric acid, evaporation to dryness, and extraction of the residue with acetone gave a product (0·65 g.), m. p. 192—194°, shown to be impure diphenic acid by infrared analysis.

Ozonolysis of Chrysene.—Chrysene, purified by chromatography on alumina followed by repeated recrystallisation from toluene, had m. p. 254—255°, and no impurities could be detected by infrared analysis. This material (2·28 g., 10 mmoles) in *sym*-tetrachoroethane (60 ml.) at 0° was treated with an equimolar quantity of ozone. Isolation of the ozonide and its decomposition with permanganate in aqueous pyridine gave 2-*o*-carboxyphenyl-1-naphthoic acid (1·40 g., 48%) as needles, m. p. 213—214° (from 10% hydrochloric acid) (Found: C, 74·0; H, 4·2%; equiv., 146. Calc. for $C_{18}H_{12}O_4$: C, 74·0; H, 4·1%; equiv., 146). Its dimethyl ester separated from light petroleum (b. p. 60—80°) in prisms, m. p. 93—94° (Found: C, 74·9; H, 5·1. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0%) (Graebe and Gnehm [20] give m. p. 199° for the acid and m. p. 90° for the ester). Decarboxylation of the acid with soda-lime gave 2-phenylnaphthalene (71%), m. p. and mixed m. p. 101—102°.

Treatment of chrysene (2·28 g.) with permanganate in pyridine gave mainly unchanged material (2·05 g.) and a small amount (0·17 g.) of chrysene-5,6-quinone.

Decomposition of chrysene ozonide with alkaline peroxide gave yellow alkali-insoluble resin, and no pure acid product could be isolated from the alkali-soluble fraction.

Oxidation of Chrysene and Chrysene-5,6-quinone with Hydrogen Peroxide–Acetic Acid.—Chrysene (7·25 g.) in acetic acid (1200 ml.) at 85—90° was treated dropwise during 3 hr. with 30% hydrogen peroxide (40 ml.) and stirred at 90° for a further 5 hr. The solvent was removed under reduced pressure and the residue extracted repeatedly with boiling 10% aqueous sodium carbonate. The alkali-insoluble portion was chromatographed on activated alumina to give unchanged chrysene (1·15 g., 14·5%) on elution with benzene–light petroleum. Elution with benzene gave a product crystallising in pale yellow needles, m. p. 191° (0·63 g.), from the same solvent (Found: C, 83·1; H, 4·3. $C_{17}H_{10}O_2$ requires C, 82·9; H, 4·1%). Infrared analysis showed the absence of hydroxyl groups and the presence of a carbonyl group. The frequency

[19] Sully, *Analyst*, 1954, **79**, 86.
[20] Graebe and Gnehm, *Annalen*, 1904, **335**, 114.

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at which the latter absorbs is too high for the substance to be a quinone. On the above evidence the compound was formulated as 2-o-*hydroxyphenyl*-1-*naphthoic acid lactone* (I).

Acidification of the alkaline extract gave a brown solid which on crystallisation from aqueous acetone (charcoal) gave 2-*o*-carboxyphenyl-1-naphthoic acid (2·9 g., 37%), m. p. 212—213°, undepressed on admixture with the acid obtained by ozonolysis and with an identical infrared spectrum.

Chrysene-5,6-quinone, m. p. 240—241°, was prepared in 57% yield by oxidation of chrysene with sodium dichromate in acetic acid.[21] Oxidation of the quinone (5 g.) with hydrogen peroxide in acetic acid gave the above lactone (0·53 g., 11%) and dicarboxylic acid (2·9 g., 51%).

Picene.—This was obtained (21%) as plates, m. p. 365° (from pyridine), by the cyclisation of 1,2-di-α-naphthylethane with aluminium chloride.[22] The dinaphthylethane was prepared as follows.

To methylmagnesium iodide [from magnesium (20·2 g.) and methyl iodide (120 g.)] in ether (500 ml.), 1-chloromethylnaphthalene [23] (124 g.) in ether (250 ml.) was added dropwise during 90 min. so that gentle refluxing was maintained. A white precipitate was gradually formed. After being heated under reflux for a further 2 hr. the mixture was cooled in ice and treated dropwise with concentrated hydrochloric acid (160 ml.) and water (700 ml.). Filtration yielded the dinaphthylethane (57·5 g., 58%), m. p. 162—163° (from ethanol–benzene). Buu-Hoï and Hoán [23] obtained a 21% yield of product, m. p. 161—162°, from 1-chloromethylnaphthalene, water, and iron powder.

A fine suspension of picene (2·78 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) was treated with 20 mmoles of ozone at 0°. Precipitation of the ozonide followed by decomposition with permanganate in aqueous pyridine gave a brown acidic resin (0·3 g.) on acidification of the hot alkaline liquor. Slow evaporation of the filtrate yielded p-*terphenyl*-2,2′,3′,2″-*tetracarboxylic acid* 2′,3′-*anhydride* (II) (1·35 g., 35%) as needles, m. p. 284—286° (decomp.), raised to 297° (decomp.) by recrystallisation from aqueous acetone (Found: C, 67·7; H, 3·3. $C_{22}H_{12}O_7$ requires C, 68·0; H, 3·1%). Infrared examination showed the presence of carboxyl groups and a 5-membered ring anhydride. Decarboxylation with soda-lime gave *p*-terphenyl (67%), m. p. and mixed m. p. 210°. Reaction of the silver salt with methyl iodide gave an amorphous *dimethyl ester*, m. p. 207° (from benzene) (Found: C, 66·6; H, 4·3. $C_{24}H_{18}O_8$ requires C, 66·4; H, 4·2%). Chromatography of the mother-liquor from this ester on activated alumina gave the *tetramethyl ester* on elution with 1 : 1 ether–benzene, and this crystallised from light petroleum (b. p. 100—120°) as needles, m. p. 115° (Found: C, 67·5; H, 4·8. $C_{26}H_{22}O_8$ requires C, 67·5; H, 4·8%).

When picene (1·39 g.) was treated with an equimolar quantity of ozone, unchanged hydrocarbon (0·61 g., 44%) and the anhydride (0·1 g., 9%) were the only isolable products.

Benzo[g]chrysene.—(*a*) Benzo[*g*]chrysene-11,12-dicarboxylic anhydride [24] (3·3 g.), copper powder (3·3 g.), and quinoline (25 ml.) were heated under reflux for 2 hr. The copper was removed and quinoline extracted with hydrochloric acid. The residue was chromatographed on activated alumina to give, on elution with light petroleum, benzo[*g*]chrysene (1·45 g., 55%), needles, m. p. 116° (from acetic acid). Bergmann and Szmuszkovicz [24] report a 40% yield by using copper and barium hydroxide.

(*b*) Cyclisation of the 1′,2-epoxide from 1-(2′-biphenylyl)-3,4-dihydronaphthalene (1·9 g.) with hydrobromic acid in acetic acid [25] gave a yellow resin from which 11,12-*dihydrobenzo*[g]-*chrysene* was obtained by elution from activated alumina with light petroleum (b. p. 60—80°). It crystallised from ethanol in cubes (1·3 g., 73%), m. p. 136—137° (Found: C, 94·2; H, 5·8. $C_{22}H_{16}$ requires C, 94·25; H, 5·75%).

Dehydrogenation of the dihydro-compound (8·7 g.) with 10% palladium–charcoal (2 g.) in *p*-cymene (150 ml.) during 24 hr. in a slow stream of carbon dioxide yielded benzo[*g*]chrysene (7·8 g., 92%), m. p. 115—116°. Bradsher and Rapoport [25] obtained a 51% yield of material, m. p. 111·5—114°, by use of sulphur and zinc dust.

A solution of benzo[*g*]chrysene (2·78 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) was

[21] Liebermann, *Annalen*, 1871, **158**, 309; Bamberger and Bergdorf, *Chem. Ber.*, 1891, **23**, 2437.
[22] Buu-Hoï and Hoán, *J. Org. Chem.*, 1949, **14**, 1023.
[23] Grummitt and Buck, *Org. Synth.*, **24**, 30.
[24] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1947, **69**, 1367.
[25] Bradsher and Rapoport, *ibid.*, 1943, **65**, 1646.

treated at 0° with an equimolar amount of ozone. The ozonide was isolated and decomposed with permanganate in aqueous pyridine. Acidification of the alkaline liquor gave a brown solid (2·37 g.). Crystallisation of this from aqueous acetone (charcoal) gave 10-*o*-*carboxyphenylphenanthrene-9-carboxylic acid* (III) (69%) as needles, m. p. 286° (decomp.) (Found: C, 78·3; H, 4·4%; equiv., 172. $C_{22}H_{14}O_4$ requires C, 77·2; H, 4·1%; equiv., 171). (It was difficult to analyse this compound owing to its extremely slow combustion.) The product had *M* (differential evaporation in pyridine),[26] 343, 346 ($C_{22}H_{14}O_4$ requires *M*, 342). Decarboxylation with copper powder and quinoline yielded 9-phenylphenanthrene (70%), m. p. and mixed m. p. 105°. The *dimethyl ester* separated from methanol in rosettes, m. p. 173° (Found: C, 77·65; H, 5·0. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%).

Dibenzo[c,g]*phenanthrene*.—This was prepared from 3,3′,4,4′-tetrahydro-1,1′-binaphthyl by Weidlich's method.[27] The final stage was improved as follows. A slow stream of carbon dioxide was passed for 2 days through a boiling mixture of 1,2,7,8-tetrahydrodibenzo[*c,g*]-phenanthrene (7·27 g.), 10% palladium–charcoal (2·5 g.), and *p*-cymene (150 ml.). The residue left on removal of catalyst and solvent was chromatographed on activated alumina. Elution with light petroleum gave dibenzo[*c,g*]phenanthrene (4·12 g., 58%) as prisms (from benzene–light petroleum), m. p. 181—182°. Elution of the column with benzene yielded benzo[*ghi*]-perylene (1·54 g., 22%) as pale yellow prisms (from xylene), m. p. 280—281°. Altman and Ginsberg [28] report an almost quantitative yield of benzo[*ghi*]perylene on use of 30% palladium–charcoal in *p*-cymene.

The hydrocarbon (2·78 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) was treated at 0° with 20 mmoles of ozone. Decomposition as usual gave *o-terphenyl-2,2″,3′,6′-tetracarboxylic acid* (IV) (2·64 g., 65%) as needles (from 10% hydrochloric acid), m. p. 302° (decomp.) (Found: C, 64·8; H, 3·65%; equiv., 102·6. $C_{22}H_{14}O_8$ requires C, 65·0; H, 3·5%; equiv., 101·6) {*tetramethyl ester*, needles [from light petroleum (b. p. 100—120°)], m. p. 125° (Found: C, 67·7; H, 4·9. $C_{26}H_{22}O_8$ requires C, 67·5; H, 4·8%)}. Decarboxylation with soda-lime yielded triphenylene (14·5%), m. p. and mixed m. p. 199°, whereas copper and quinoline gave *o*-terphenyl (60%), m. p. and mixed m. p. 57°. Distillation of *o*-terphenyl with soda-lime gave 5% of triphenylene.

Ozonolysis of Triphenylene.—Triphenylene [29] (2·28 g., 10 mmoles) was ozonised (2 mol.) in *sym*-tetrachloroethane (60 ml.) at 0°. Decomposition, acidification of the alkaline liquor, and crystallisation of the precipitate from acetic anhydride (charcoal) gave phenanthrene-9,10-dicarboxylic anhydride (0·55 g., 22%), yellow needles, m. p. and mixed m. p. 315—316° (Szmuszkovicz and Modest [30] give m. p. 316—317°). The acidic filtrate was evaporated to dryness, and the residue extracted with boiling acetone to give diphenic acid (0·19 g., 7·8%), m. p. and mixed m. p. 229° (correct infrared spectrum).

Decomposition of the ozonide with alkaline peroxide as described for phenanthrene ozonide gave the anhydride and diphenic acid in similar yield.

Absorption of 3 or 4 mol. of ozone led to resins from which diphenic acid (16% and 20% respectively) was isolated.

Ozonolysis of Benz[a]*anthracene*.—Purified benz[*a*]anthracene,[31] m. p. 160° (2·28 g., 10 mmoles), in *sym*-tetrachloroethane (60 ml.) at 0° was treated with 1 mol. of ozone. The ozonide was precipitated by addition of light petroleum (b. p. 40—60°) and the filtrate was distilled in steam, to give a brown residue (1·1 g.). Chromatography of this material on activated alumina gave unchanged hydrocarbon (0·64 g., 28%) and benz[*a*]anthracene-7,12-quinone (0·24 g., 13%), m. p. 169° (Graebe [32] gives m. p. 169—170°), on elution with light petroleum (b. p. 60—80°) and chloroform respectively. Decomposition of the ozonide with permanganate in aqueous pyridine, followed by acidification of the alkaline liquor, gave a sticky yellow resin. Slow evaporation of a benzene solution of this material gave a pale yellow solid which yielded 3-*o*-carboxyphenyl-2-naphthoic acid (0·24 g., 11·4%), needles (from 10% hydrochloric acid), m. p. 250° (Found: C, 74·1; H, 4·3%; equiv., 146. Calc. for $C_{18}H_{12}O_4$:

[26] Baldes, *J. Scientific Inst.*, 1934, **11**, 223; *Biodynamica*, 1939, **46**, 1; **47**, 1; Blayden, Northern Coke Research Committee Progress Report, No. **48**, 24; No. **49**, 15.
[27] Weidlich, *Ber.*, 1938, **71**, 1203.
[28] Altman and Ginsberg, *J.*, 1959, 466.
[29] Copeland, Dean, and McNeil, *J.*, 1960, 1687.
[30] Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1948, **70**, 2542.
[31] Fieser and Hershberg, *ibid.*, 1937, **59**, 2502.
[32] Graebe, *Annalen*, 1905, **340**, 259.

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C, 74·0; H, 4·1%; equiv., 146). The dimethyl ester separated from light petroleum (b. p. 40—60°) in rhombs, m. p. 87° (Found: C, 75·2; H, 5·2. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0%). Cook and Schoental [9] give m. p. 249—250° for the acid and m. p. 86—87·5° for the ester. Decarboxylation of the acid with soda-lime gave 2-phenylnaphthalene (66%), m. p. and mixed m. p. 101—102°.

Absorption of 2 mol. of ozone gave 17% each of the quinone and diacid; no unchanged hydrocarbon could be isolated.

Absorption of 3 mol. yielded an ozonide which decomposed spontaneously on drying.

Treatment of benz[*a*]anthracene (2·28 g.) with 1 mol. of ozone and decomposition of the ozonide with alkaline peroxide yielded unchanged hydrocarbon (0·72 g., 31·6%) and the quinone (0·4 g., 21·6%), but no acid.

Oxidation of Benz[a]*anthracene.*—Benz[*a*]anthracene (5 g.) was oxidised in acetic acid (300 ml.) with 30% hydrogen peroxide (25 ml.) as described for chrysene. Chromatography of the alkali-insoluble material on activated alumina gave the quinone (2·1 g., 36%) on elution with chloroform–benzene. Acidification of the alkali-soluble fraction gave 3-*o*-carboxyphenyl-2-naphthoic acid (1·31 g., 20·5%), m. p. and mixed m. p. 250°.

Ozonolysis of Benz[a]*anthracene-7,12-quinone.*—The quinone (2·58 g., 10 mmoles) in chloroform (60 ml.) at −20° was treated with 20 mmoles of ozone. After replacement of the oxygen by nitrogen, 10% aqueous sodium hydroxide (20 ml.) and 30% hydrogen peroxide (10 ml.) were added. The mixture was heated at 60° with stirring for 1 hr. The solvent was removed and the red solution acidified with 10% hydrochloric acid, to give a yellow precipitate (2·37 g., 80%), m. p. 320—322°, of anthraquinone-1,2-dicarboxylic acid. Crystallisation from boiling water gave long yellow needles, m. p. 270° (sealed tube), m. p. 330° (open tube) (Found: C, 64·9; H, 2·9. Calc. for $C_{16}H_8O_6$: C, 64·9; H, 2·7%). The dimethyl ester separated in yellow prisms (from ethyl acetate), m. p. 210—211° (Found: C, 66·6; H, 3·8. Calc. for $C_{18}H_{12}O_6$: C, 66·7; H, 3·7%). The acid yielded anthraquinone (91%) on decarboxylation with copper and quinoline.

The authors thank Mr. G. A. Vaughan for the analyses, Mr. W. G. Wilman for the infrared examinations, Mr. F. Brook for technical assistance, and Dr. H. Boer for his helpful comments.

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242. *Liquid Hydrogen Chloride as an Ionizing Solvent. Part III.*[1] *Solubilities and Reactions of Some Derivatives of Groups IV, V, and VI.*

By M. E. PEACH and T. C. WADDINGTON.

The conductivities of various derivatives, mainly organic, of elements of Groups IV, V, and VI in anhydrous liquid hydrogen chloride have been measured. All these compounds would act as solvobases, and conductivity titrations have been performed by using boron trichloride as an acid.

THIS paper concerns first compounds of the type Ph_3MX (M is an element of Group IV and X = Cl or OH), and attempts to prepare the ions Ph_3M^+. The Ph_3C^+ ion is well characterised [2,3] and has been found in protonic solvents such as sulphuric acid [2] and in non-protonic solvents such as sulphur dioxide.[4] No cases of the ion Ph_3Si^+ have yet been reported,[5,6] although the recently prepared $Ph_3Si{\cdot}ClO_4$ may contain this ion.[7] No other

[1] Parts I and II, Waddington and Klanberg, *J.*, 1960, 2329, 2332.
[2] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.
[3] Sharp and Sheppard, *J.*, 1957, 674.
[4] Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1674.
[5] Sharp, "Advances in Fluorine Chemistry," Butterworth Scientific Publ., London, 1960, Vol. I, p. 96.
[6] Gillespie and Robinson, "Advances in Inorganic and Radiochemistry," Academic Press Inc., New York, 1959, Vol. I, p. 385.
[7] Wannagat, Braudmair, Leihr, and Neiderprüm, *Z. anorg. Chem.*, 1959, **302**, 185.

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ions of type Ph_3M^+ have been prepared but the somewhat similar ion Me_3Sn^+ has been detected in sulphuric acid [6] and in the compound $Me_3Sn^+[BF_3{\cdot}CF_3]^-$.[8]

Next, it concerns derivatives of elements of Group V, of the type Ph_3M, it being hoped to protonate the element to give Ph_3MH^+ and isolate this as the tetrachloroborate. The ions Ph_3NH^+ and Ph_3PH^+ have been found in sulphuric acid,[6] but there is no evidence for Ph_3AsH^+. After the success of the experiments in liquid hydrogen chloride with phosphine [1] attempts were made to prepare the arsonium ion, AsH_4^+.

Finally, it concerns elements of Group VI, but here only oxygen and sulphur were studied. The compounds were of the type ROR′, where R and R′ were H, Me, or Ph. The object was to make protonated derivatives; in sulphuric acid this is complicated by sulphonation.[2] The effect of the substituents on the electron-availability and hence proton-acceptability can be assessed very roughly by the magnitude of the equivalent conductivities.

Experimental

The apparatus and techniques used have been described.[1]

Boron trichloride or trifluoride was introduced from the gas phase, in known amounts, by freezing on top of the frozen solution of other reactants. Measured volumes of liquid materials were obtained by use of an Agla micrometer syringe.

The reactions in the liquid hydrogen chloride were followed conductometrically, or by weighing a cell before and after reaction. The conductivity cells were made of Pyrex glass, vacuum-tight metal-to-glass seals being obtained by using tungsten wire on to which a platinum electrode had been silver-soldered. In solvolyses where one material was precipitated, a Y-shaped apparatus was used, attached to a ball-and-socket joint; the reaction was performed in one limb and the supernatant liquid was then decanted into the other; the hydrogen chloride was then evaporated and the product analysed.

Vapour-pressure measurements were performed by means of liquid in a small bulb attached to a spiral gauge. The dead-space was reduced to a minimum (*ca.* 10—15 ml.), and pressures were read by using the spiral gauge as a null-point instrument.

Chloride was determined by the Volhard method, and boron acidimetrically as the mannitol–borate complex; carbon, hydrogen, and nitrogen were determined by microcombustion. Results for chloride and boron may be slightly low as the materials usually reacted violently with water.

Arsine was made by reduction of arsenic trichloride with lithium aluminium hydride in anhydrous ether. Diphosphine was made by a slight modification of Evers and Street's method.[9] Other reagents were available commercially or were prepared by our colleagues in other researches.

Infrared measurements were taken on a Perkin-Elmer 21 double-beam continuously recording spectrophotometer with rock-salt or potassium bromide optics: some of the less important spectra were taken on a Perkin-Elmer Infracord instrument.

Conductivities.—These results are shown in Table 1.

Group IV, *Compounds* Ph_3MX.—Triphenylmethyl chloride dissolved in the liquid hydrogen chloride to a yellow, highly conducting solution. The colour is characteristic of the Ph_3C^+ ion and the ions present are formed by the reaction $Ph_3CCl + HCl \longrightarrow Ph_3C^+ + HCl_2^-$. The solution was titrated against boron trichloride and a break in the curve was found at a 1 : 1 molar ratio. The yellow solid isolated was $Ph_3C^+BCl_4^-$ (Found: C, 60·5; B, 2·7; Cl, 34·7. Calc. for $C_{19}H_{10}BCl_4$: C, 59·0; B, 2·7; Cl, 35·8%).

Triphenylsilyl chloride was very sparingly soluble and it was not possible to form an adduct from it with boron trichloride; the product, after treatment of the triphenylsilyl chloride with a stoicheiometric excess of boron trichloride, contained less than 0·1% of boron.

Triphenylgermanyl chloride was sparingly soluble in liquid hydrogen chloride. No adduct was produced with boron trichloride and the compound appears to have disproportionated.

Analyses for carbon were unsatisfactory as the compound readily decomposes in moist air: because there was only a small amount of material available it was not possible to repeat the experiment in a weighed vessel.

[8] Chambers, Clark, and Willis, *Proc. Chem. Soc.*, 1960, 114.
[9] Evers and Street, *J. Amer. Chem. Soc.*, 1956, **78**, 5727.

Triphenylstannyl chloride was almost insoluble and its conductivity changed with time. It disproportionated quantitatively in 2 hr. to dichlorodiphenylstannane (Found: C, 41·2; H, 3·0; Cl, 19·6, 19·7; loss of wt., 10·8%. Calc. for $C_{12}H_{10}Cl_2Sn$: C, 41·9; H, 2·9; Cl, 20·6; loss of wt., 10·9%).

TABLE 1. *Specific and molar conductances of compounds in liquid hydrogen chloride at −95°.*

Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} $cm.^{-1}$)	Molar conductance ($cm.^2$ ohm^{-1} $mole^{-1}$)	Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} $cm.^{-1}$)	Molar conductance ($cm.^2$ ohm^{-1} $mole^{-1}$)
Ph_3CCl	0·15	$0·518 \times 10^{-4}$	34·2	H_2O	Satd.	$4·3 \times 10^{-6}$	—
	0·25	$1·064 \times 10^{-4}$	42·9	H_2S	,,	$2·8 \times 10^{-6}$	—
Ph_3SnCl	Satd.	$1·53 \times 10^{-6}$	—	MeOH	0·51	$68·7 \times 10^{-6}$	0·13
Ph_3GeCl	,,	$1·11 \times 10^{-6}$	—	MeSH	0·27	$14·7 \times 10^{-6}$	0·054
Ph_3SnCl *	,,	$0·35 \times 10^{-6}$	—	PhOH	0·25	$4·75 \times 10^{-6}$	0·019
Ph_3PbCl	,,	$2·2 \times 10^{-6}$	—	PhSH	0·39	$11·7 \times 10^{-6}$	0·030
Ph_3N	0·22	$1·50 \times 10^{-3}$	6·85	PhOMe	0·32	$6·8 \times 10^{-6}$	0·021
Ph_3N	0·49	$4·67 \times 10^{-3}$	9·54	PhOPh	0·38	$0·66 \times 10^{-6}$	0·0017
Ph_3N	0·75	$7·14 \times 10^{-3}$	9·48	PhOPh	0·48	$0·54 \times 10^{-6}$	0·0012
Ph_3P	0·31	$6·51 \times 10^{-3}$	21·1	PhSPh	0·25	$38·7 \times 10^{-6}$	0·15
Ph_3As	0·17	$5·07 \times 10^{-3}$	30·7	MeOMe	0·26	$114·4 \times 10^{-6}$	0·43
Ph_3As	0·20	$7·70 \times 10^{-3}$	39·3	MeSMe	0·44	$5·16 \times 10^{-3}$	11·8
Ph_3As	0·30	$11·88 \times 10^{-3}$	39·5	MeSMe	0·35	$3·95 \times 10^{-3}$	11·3
Ph_3Sb *	Satd.	$8·9 \times 10^{-6}$	—	MeSMe	0·29	$2·90 \times 10^{-3}$	10·1
Ph_3Bi *	,,	$0·31 \times 10^{-6}$	—	$BiCl_3$	Satd.	$0·46 \times 10^{-6}$	—
P_2H_4	,,	$2·17 \times 10^{-5}$	—				
P_2H_4	,,	$2·13 \times 10^{-5}$	—				
AsH_3 †	,,	$2·63 \times 10^{-5}$	—				
AsH_3 †	,,	$1·11 \times 10^{-4}$	—				
NH_4Cl	,,	$1·3 \times 10^{-6}$	—				
$N_2H_4.2HCl$	,,	$1·0 \times 10^{-6}$	—				
$Ph_2N{\cdot}NH_2$	0·37	$0·852 \times 10^{-3}$	2·30				

* Initial values as decomposition occurs. † Values at −111·6°.

Triphenylplumbyl chloride gave a yellow solution and a copious orange precipitate. It disproportionated but it is uncertain what the products are. The reaction may be impeded by the surface precipitation of lead tetrachloride.[1] After this chloride had been in liquid hydrogen chloride for 2 hr. a white solid was obtained on removal of the solvent (Found: C, 42·9; H, 3·1; loss of wt., 4·5. Calc. for $C_{18}H_{15}ClPb$: C, 45·6; H, 3·2. Calc. for $C_{18}H_{10}Cl_2Pb$: C, 33·4; H, 2·3; loss of wt., 8·8%).

Triphenylmethanol gave a red solution and a white precipitate. The soluble product of a solvolysis reaction was triphenylmethyl chloride (Found: Cl, 12·7. Calc. for $C_{19}H_{15}Cl$: Cl, 12·7%).

Triphenylsilanol was sparingly soluble. A solvolysis experiment showed that a little of the chloride had been formed (Found: Cl 0·8. Calc. for $C_{18}H_{15}ClSi$: Cl, 12·0%).

Group V.—(*a*) Triphenylamine was readily soluble, giving a pale brown or a deep blue solution. Pale brown solutions (0·29—0·51M) were obtained with freshly purchased material: a sample freshly sublimed *in vacuo* and then kept for 6 months gave a blue solution. The colour is not a function of concentration as 0·28—1·0M-solutions were all blue. The material acted as a strong base and was titrated against boron trichloride: the titration curve (Fig. 1) shows a sharp break at 1 : 1 molar ratio. The product was white, but this soon became blue in a dry box: it was *triphenylammonium tetrachloroborate* (Found: B, 2·5; Cl, 35·2; N, 3·8. $C_{18}H_{16}BCl_4N$ requires B, 2·7; Cl, 35·5; N, 3·5%).

Triphenylphosphine was readily soluble, giving a pale yellow solution. A conductivity titration against boron trichloride showed a sharp break at a 1 : 1 molar ratio. The infrared absorption included a weak PH^+ frequency [10] at 2300—2400 $cm.^{-1}$; its composition as *triphenylphosphonium tetrachloroborate* was confirmed by analysis (Found: B, 2·4; C, 35·8. $C_{18}H_{16}BCl_4P$ requires B, 2·6; Cl, 34·1%).

Triphenylarsine was readily soluble, giving a slightly brown solution: the solubility limit

[10] Shelden and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 2117.

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was about 1M. It was a strong base and the conductivity titration against boron trichloride, shown in Fig. 2, gave a sharp break at the 1 : 1 molar ratio. The product at room temperature was the triphenylarsine–boron trichloride *adduct*, Ph_3As,BCl_3 (Found: B, 2·3; Cl, 25·4, 25·7; increase in wt., 38·5. $C_{18}H_{15}AsBCl_3$ requires B, 2·6; Cl, 25·1; increase in wt., 38·3%). The white solid residue obtained at −95° gave off slightly more than a mol. of hydrogen chloride at about −25°, but accurate quantitative investigation at this temperature was impossible. From the similarity of the conductivity curve to those of triphenylamine and boron trichloride the following reactions have been inferred:

$$Ph_3As + 2HCl \longrightarrow Ph_3AsH^+ + HCl_2^-$$
$$Ph_3AsH^+ + BCl_3 + HCl_2^- \longrightarrow Ph_3AsH^+BCl_4^- + HCl$$

One mol. of triphenylarsine and methanesulphonic acid were mixed in the solvent: the infrared spectrum of the solid product obtained on removal of the solvent showed the frequencies of

FIG. 1. *Conductimetric titration*: 0·75M-Ph_3N–BCl_3.

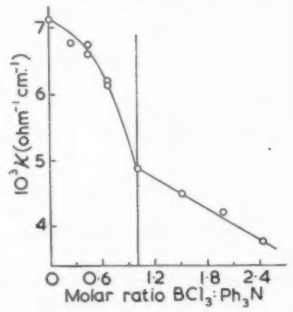
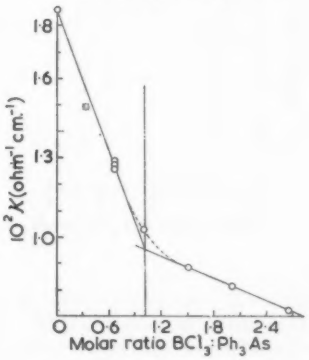


FIG. 2. *Conductimetric titration*: 0·30M-Ph_3As–BCl_3.



the methanesulphonate ion, loss of O–H frequencies, and a very weak band in the 2400 cm.$^{-1}$ region which may be due to the AsH^+ stretching vibration.

Triphenylstibine was incompletely soluble, giving a colourless solution. It slowly disproportionated and after 4 hr. had lost 19·5% of its weight ($Ph_3Sb \longrightarrow SbCl_3$; loss of wt., 35·4%). It was not possible to identify the product (Found: Cl, 13·4. Calc. for Cl_3Sb: Cl, 46·6%). The slowness of the reaction may be due to the formation of insoluble antimony trichloride [1] on the surface of the triphenylstibine.

Triphenylbismuthine was almost completely insoluble and slowly disproportionated (Found, in the product: C, 6·5; H, 1·6; Cl, 26·7; loss of wt., 22·1. Calc. for $BiCl_3$: Cl, 33·7; loss of wt., 28·3%).

(*b*) Ammonium chloride was sparingly soluble and attempts to prepare the tetrachloroborate failed (Found: B, 0; Cl, 65·6. Calc. for NH_4Cl: Cl, 66·2%).

Hydrazinium dichloride was sparingly soluble, and because of this no attempt was made to cause it to react with boron trichloride.

Hydrazobenzene gave a deep red solution and a yellow precipitate: the conductivity was time-variable. The infrared spectrum of the product showed that the hydrazobenzene had been converted into benzidine: $(NHPh\cdot)_2 + 4HCl \longrightarrow (\cdot C_6H_4\cdot NH_3^+)_2(HCl_2^-)_2$.

NN-Diphenylhydrazine gave a yellow solution. The conductivity titration against boron trichloride, shown in Fig. 3, gave a sharp break at the 1 : 1 molar ratio: the big drop in conductivity on addition of boron trichloride is due to precipitation. The light blue product was NN-*diphenylhydrazinium tetrachloroborate* (Found: C, 43·7; H, 3·9; B, 3·1; Cl, 4·20; N, 8·9. $C_{12}H_{13}BCl_4N_2$ requires C, 42·7; H, 3·9; B, 3·2; Cl, 42·0; N, 8·3). The infrared spectrum in the potassium bromide region showed tetrachloroborate frequencies at 693 and 670 cm.$^{-1}$.[11] In the rock-salt region NH bands were observed at 2680, 2460, and 1568

[11] Kynaston, Larcombe, and Turner, *J.*, 1960, 1772.

cm.$^{-1}$. Although these data are insufficient to assign the proton to a specific nitrogen atom the compound probably has the structure $Ph_2N{\cdot}NH_3^+BCl_4^-$.

Diphosphine was not very soluble in liquid hydrogen chloride. Conductivity titrations with boron trifluoride and boron trichloride showed no breaks: addition of 0·1 mol. of boron trichloride gave a polymer. As diphosphine decomposes in the gas phase to phosphine and a yellow material no further experiments were performed.

Arsine was not very soluble and gave a brown precipitate, possibly arsenic. A vapour-pressure diagram of arsine and hydrogen chloride at −95° showed a slight break at the 1 : 1 molar ratio. The infrared spectrum of gas in equilibrium with a liquid mixture of arsine (1 mol.) and hydrogen chloride (4 mols.) at −95° showed an appreciable concentration of

FIG. 3. *Conductimetric titration*: 0·37M-$Ph_2N{\cdot}NH_2$–BCl_3.

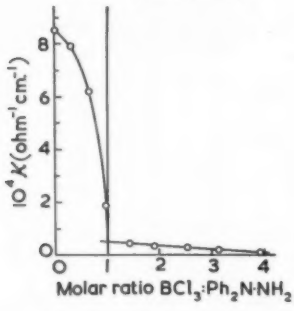
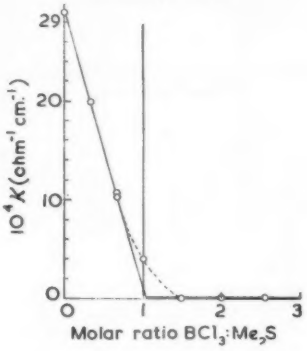


FIG. 4. *Conductimetric titration*: 0·29M-Me_2S–BCl_3.



arsine, which was considerably reduced when just over a mol. of boron trichloride had been added. This indicates that AsH_3,BCl_3 or $AsH_4^+BCl_4^-$ is less dissociated than AsH_3,HCl. Conductivity titrations with boron trifluoride and boron trichloride are unsatisfactory but both show turning points at the 1 : 1 molar ratio. No solid product was obtained at room temperature; the gas given off on warming was a mixture of hydrogen chloride, arsine, and boron trihalide.

Group VI*: Oxygen and Sulphur Compounds.*—Hydrogen sulphide was sparingly soluble, giving a white precipitate and a colourless solution. On addition of boron trichloride it became more soluble, and a conductivity titration showed a sharp initial rise, followed by a slow fall. A trace of insoluble residue was left at room temperature: this was not sulphur or hydrogen polysulphide as the infrared spectrum showed peaks at 3200 and 1190 cm.$^{-1}$.

Methanol gave a colourless solution. Conductivity titration with boron trichloride yielded a smooth curve. A liquid residue was obtained on evaporation at −95°; this was probably dimethoxyboron chloride, m. p. −87·5° [12] (Found: *M*, 108·6. Calc. for $C_2H_6BClO_2$: *M*, 108·4).

Methanethiol was readily soluble. With boron trichloride, it gave an adduct, which melted at about −20° (decomp.) (Found: B, 5·5; Cl, 58·1%; Cl/B, 10·5; increase in wt., 246%. Calc. for CH_4BCl_3S: B, 6·5; Cl, 64·4%; Cl/B, 9·84; increase in wt., 244%). When kept in the dry box it remained liquid and it was not possible to obtain $(MeS{\cdot}BCl_2)_2$, m. p. 72·7°, which had previously been found.[13]

Dimethyl ether gave a highly conducting solution. Titration with boron trichloride showed a break at 1 : 1 molar ratio; from the low equivalent conductivity at this point (0·012 mho cm.^{2} mole^{-1}) it is assumed that an adduct has been formed in solution. This was confirmed as on warming to room temperature little gas (0·03 mole) was given off by the product (Found: B, 6·0; Cl, 65·1. Calc. for $C_2H_6BCl_3O$: B, 6·6; Cl, 65·1%).

Dimethyl sulphide was the most highly conducting oxygen or sulphur compound investigated Titration with boron trichloride showed a sharp break at the 1 : 1 molar ratio (Λ 0·033 mho cm.^{2}

[12] Wiberg and Sätterlen, *Z. anorg. Chem.*, 1931, **202**, 1.
[13] Goubeau and Wittmeier, *Z. anorg. Chem.*, 1952, **270**, 16.

mole^{-1}) (Fig. 4). The product had a dissociation pressure of about 8 mm. at room temperature; analysis suggests that it was the methyl sulphide–boron trichloride adduct (Found: C, 5·6; Cl, 57·8%; Cl/B, 10·5. Calc. for $C_2H_6BCl_3S$: B, 6·0; C, 59·4%; Cl/B, 9·8). As only a small amount of gas was given off on warming to room temperature it can be assumed that the adduct was formed in the solution.

Phenol was soluble, up to about 1M-solutions. With boron trichloride, products of the type $(PhO)_xBCl_{3-x}$ were produced. The product gave off 0·15 mol. of gas on warming and its infrared spectrum showed loss of OH frequencies and appearance of frequencies at 1350 (B–O stretching?), 710, and 739 cm.$^{-1}$ (B–Cl). Analysis of the liquid product indicated it to be a mixture of $PhO{\cdot}BCl_2$ and $(PhO)_2BCl$.

Thiophenol gave a poorly conducting solution: titration with boron trichloride produced a curve similar to that for hydrogen sulphide. The greenish, slimy product gave off 0·86 mole of a mixture of hydrogen chloride and boron trichloride at room temperature. It appears to decompose into $PhS{\cdot}BCl_2$ and $(PhS)_2BCl$ (cf. the phenol product).

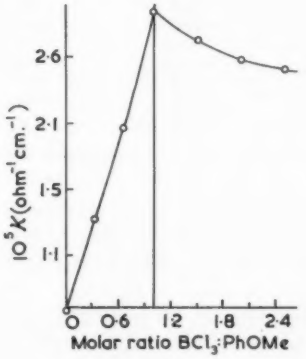


FIG. 5. *Conductimetric titration*: 0·32M-PhOMe–BCl_3.

Anisole gave a pale pink solution. Titration with boron trichloride is shown in Fig. 5: there is a break at the 1 : 1 molar ratio (Λ 0·093). The slightly purplish solid product had a vapour pressure of 15—20 mm. at room temperature, the vapour being boron trichloride. It melted to a purple liquid. Immediate weight analysis showed it to be the anisole–boron trichloride adduct (Found: increase in wt., 102. Calc. for $C_6H_5BCl_2O$: increase in wt., 118%). No methyl chloride was given off at room temperature.

Diphenyl ether gave a very poorly conducting solution. Titration with boron trichloride gave a smooth curve. On warming to room temperature the solution gave 0·56 mol. of a mixture of hydrogen chloride and boron trichloride, the product being diphenyl ether (Found: B, 0·9; Cl, 0·4%): this was confirmed by the infrared spectrum (cf. refs. 14 and 15).

Diphenyl sulphide gave a purple solution. Titration with boron trichloride gave a smooth curve: the greyish product gave off 0·18 mol. of boron trichloride at room temperature. The product fumed in the dry box and is probably the adduct which readily dissociates (Found: B, 2·5; Cl, 22·8; Cl/B, 9·0. Calc. for $C_{13}H_{10}BCl_3S$: B, 3·6; Cl, 35·1%; Cl/B, 9·7).

DISCUSSION

Use of Conductivity Titrations.—The equivalent conductivities at the beginning and equivalence point are shown for seven materials in Table 2 (in all cases boron trichloride is being used as an acid). From these figures it is seen that when an adduct is the main product the conductivity is usually low at the equivalence point and had changed very considerably. It can therefore be deduced that, from triphenylarsine, the salt $Ph_3AsH^+BCl_4^-$ is obtained at the equivalence point, whereas from methyl sulphide the

[11] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.
[13] Healy and Palka, *J. Chem. Phys.*, 1958, **28**, 211.

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adduct Me_2S,BCl_3 is formed. It is also seen from Figs. 1, 2, and 4 that when an adduct is formed the curve is smooth in the 1/1 region whereas a sharp break occurs when tetrachloroborates are produced.

Colours of Solutions.—The only coloured solutions were from some phenyl derivatives, *e.g.*, anisole, triphenylphosphine. This may be due to slight protonation of the aromatic nucleus as various compounds of aromatic hydrocarbons are highly coloured, *e.g.*, $ArH_2^+AlCl_4^-$,[16] $ArH_2^+AlBr_4^-$,[17] $ArH_2^+BF_4^-$.[18] For triphenylamine a blue or brown colour was observed: it has previously been reported as blue.[19] This blue colour may be due to ions of the type Ar_3N^+, as $(p\text{-}C_6H_4Me)_3N^+ClO_4^-$ is blue.[20]

TABLE 2. *Conductivities at* 1 : 1 *molar ratio for boron trichloride titrations*

Base	Λ of base (mho cm.² mole⁻¹)	Λ at 1/1 ratio (mho cm.² mole⁻¹)	Ratio, Λ pure base/Λ 1/1	Product in solution
Ph_3N	12·6	7·8	1·62	$Ph_3NH^+BCl_4^-$
Ph_3As	39·5	20·4	1·94	$Ph_3AsH^+BCl_4^-$
Me_2O	0·43	0·012	25·8	Me_2O,BCl_3
Me_2S	10·05	0·033	304·6	Me_2S,BCl_3
Ph_3CCl	42·9	20·0	2·15	$Ph_3C^+BCl_4^-$
Ph_3P	21·1	15·6	1·35	$Ph_3Ph^+BCl_4^-$
Ph_3As *	39·5	37·9	1·04	$Ph_3AsH^+Me{\cdot}SO_3^-$

* On use of methanesulphonic acid.

Group IV *Compounds.*—The formation of a salt $Ph_3C^+BCl_4^-$ and the solvolysis of triphenylmethanol is probably due to the stability of the carbonium ion. The driving force in the latter reaction may be the insolubility of hydroxonium chloride: $Ph_3C{\cdot}OH + 4HCl \longrightarrow Ph_3C^+ + HCl_2^- + H_3O^+Cl^-$. The absence of solvolysis of the silanol must mean that it does not occur by an ionic mechanism: this should be contrasted with the method of formation of the triphenylsilyl chloride by bubbling gaseous hydrogen chloride through an ethereal solution of the silanol.[21] In all the other cases disproportionation occurs to varying extents; this is not really surprising since triphenyl-lead chloride reacts quantitatively, to give diphenyl-lead dichloride, when hydrogen chloride is passed into its benzene solution.[22] The following disproportionations have also been observed with somewhat similar tin compounds:

$$(p\text{-}MeO{\cdot}C_6H_4)_2SnPh_2 \xrightarrow[HCl]{\text{Conc. aq.}} Ph_2SnCl_2 \quad \text{(ref. 23)}$$

$$Ph_2Sn{\cdot}OH \xrightarrow{\text{Dry HCl}} Ph_2SnCl{\cdot}OH \quad \text{(ref. 24)}$$

However, not all reactions proceed similarly in liquid and in aqueous hydrogen chloride; *e.g.*, stannic and plumbic chloride are both insoluble [1] in liquid hydrogen chloride but form complex ions MCl_6^{2-} in the concentrated aqueous acid.

Group V *Compounds.*—With the triphenyl derivatives of the elements of higher atomic weight disproportionation occurs as with Ph_3MCl. In the series nitrogen, phosphorus, and arsenic, it is noteworthy that the conductivity and hence, presumably, basic strength, increases in that order, perhaps owing to the increasing size of the central atom. The

[16] Brown and Frith, *Proc. Indiana Acad. Sci.*, 1953, **63**, 740.
[17] Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6268.
[18] Olah and Kuhn, *Nature*, 1956, **178**, 1344.
[19] Kemmitt, Nuttall, and Sharp, *J.*, 1960, 40.
[20] Weitz and Schwechten, *Ber.*, 1926, **59**, 2307; 1927, **60**, 545.
[21] Kaus and Rosen, *J. Amer. Chem. Soc.*, 1925, **47**, 2746.
[22] Gilman and Robinson, *J. Amer. Chem. Soc.*, 1929, **51**, 3112.
[23] Bobashinkaya and Kochesharka, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **8**, 1850; *Chem. Zentr.*, 1940, I, 359.
[24] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1055.

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product $Ph_3PH^+BCl_4^-$ is similar to the known salt [25] $Et_3PH^+BCl_4^-$. With arsine the species in the solution is undoubtedly Ph_3AsH^+ and the material at the end-point of the titration is $Ph_3AsH^+BCl_4^-$, but this loses hydrogen chloride on warming to room temperature. Previous attempts to make the similar salt $Me_3AsH^+BCl_4^-$ by condensing hydrogen chloride on to Me_3AsBCl_3 failed [25] as hydrogen chloride was recovered when the mixture warmed to room temperature: this case may be similar to that of triphenylarsine and a salt $Me_3AsH^+BCl_4^-$ may be present at low temperatures.

After the success of the triphenylarsine and phosphine experiments,[1] arsine itself was studied. Failure to produce the arsonium ion is, however, not surprising as the dissociation pressure of phosphonium chloride is ~1 atm. at −40°, and 10 mm. at −80°, and of ammonium chloride is ~250 mm. at 300°. The results probably indicate slight formation of $AsH_4^+Cl^-$ in liquid hydrogen chloride, and greater stability of the arsonium ion in solution when boron trichloride is also present.

The failure to make ammonium tetrachloroborate must be due to the extreme insolubility of ammonium chloride, as the salt has been prepared in 91% yield by grinding the reactants in chloroform.[11]

With hydrazine no attempt was made to prepare the tetrachloroborate after the failure with ammonium chloride. It was possible to make a substituted hydrazinium tetrachloroborate, $Ph_2N{\cdot}NH_2,HBCl_4$. It is not possible to assign a complete structure from the infrared spectrum but the product certainly contains the tetrachloroborate ion.

Group VI *Compounds.*—In this series, remarkably, no stable protonated derivative was formed with boron trichloride; the adducts and their decomposition products were produced. All the compounds that contained an active hydrogen readily lost hydrogen chloride, in accord with previous observations, for, *e.g.*, methanol–boron trichloride and phenol–boron trichloride.[26]

Various protonated derivatives with hydrogen chloride have previously been reported, *e.g.*, $(MeOH)_3(HCl)_2$,[27] m. p. −64°, $MeOH,HCl$,[28] m. p. −62°, $Me_2O,5HCl$,[28] and Me_2O,HCl in the gas phase; [29,30] so it seems surprising the onium salts are not formed. Absence of protonation of diphenyl ether has also been observed in sulphuric acid and is attributed to forms such as $Ph{\cdot}O^+{:}C_6H_4^-$, and it is also not possible to form boron trichloride adducts.[14,15]

The present work differs from earlier work in that phenol and anisole were previously reported to be insoluble in hydrogen chloride.[31] It was not possible to promote fission of anisole, to give $PhO{\cdot}BCl_2$ and methyl chloride—the latter was not evolved even when the compound melted: from a previous report [32] it is not quite clear when fission is supposed to occur. Phenoxyboron chlorides from phenol and boron trichloride dissociate readily, phenoxyboron dichloride at −15°, the ultimate products being triphenyl borate and boron trichloride.[14]

A general study of the equivalent conductivities shows them to increase in the order diphenyl ether, phenol, anisole; this must be due to the relative electron-releasing powers, $Ph < H < Me$. This conclusion is, in general, confirmed for the series diphenyl ether, water, and dimethyl ether, and diphenyl sulphide, hydrogen sulphide, and dimethyl sulphide.

One of us (M. E. P.) acknowledges his indebtness to the D.S.I.R. for a maintenance grant.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 22nd,* 1960.]

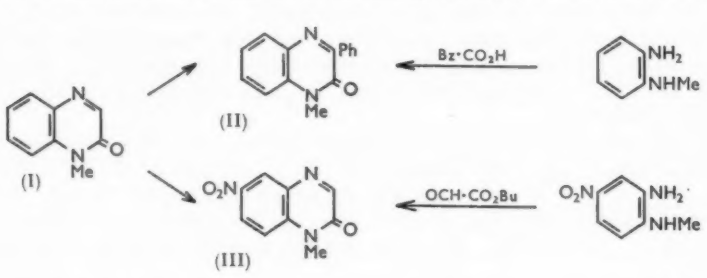
[25] Hewitt and Holliday, *J.*, 1953, 530.
[26] Gerrard and Lappert, *Chem. Rev.*, 1958, **58**, 1081.
[27] McIntosh, *J. Amer. Chem. Soc.*, 1906, **28**, 590.
[28] Maas and McIntosh, *J. Amer. Chem. Soc.*, 1913, **35**, 535.
[29] Gladisher and Syrkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1938, **20**, 145.
[30] Maas and Morrison, *J. Amer. Chem. Soc.*, 1923, **45**, 1675.
[31] Maas and McIntosh, *J. Amer. Chem. Soc.*, 1911, **33**, 70.
[32] Gerrard and Lappert, *J.*, 1952, 1486.

243. *Quinoxalines and Related Compounds. Part V.*[1] *Some Experiments with 1,2-Dihydro-2-oxoquinoxalines.*

By G. H. W. Cheeseman.

Although 1,2-dihydro-1-methyl-2-oxoquinoxaline (I) can be methylated and hydroxylated at position 3, conditions have now been found under which it undergoes phenylation at position 3 and nitration at position 6. A number of 3-methyl-, 3-hydroxy-, and 6-nitro-quinoxalines have been prepared by substitution procedures. *E.g.*, nitration of 2-hydroxyquinoxaline (1,2-dihydro-2-oxoquinoxaline) gave 2-hydroxy-6-nitroquinoxaline, previously a difficultly accessible compound.

1,2-Dihydro-1-methyl-2-oxoquinoxaline (I) formed an aryl derivative when treated with an aqueous solution of benzene- or *p*-nitrobenzene-diazonium chloride. Proof that phenylation had taken place at position 3 was obtained by the identity of the product with 1,2-dihydro-1-methyl-2-oxo-3-phenylquinoxaline (II) synthesised unambiguously from *N*-methyl-*o*-phenylenediamine and phenylglyoxylic acid. This product was also obtained by methylation of 2-hydroxy-3-phenylquinoxaline with methyl sulphate and alkali. Stannous chloride and hydrochloric acid reduced the *p*-nitrophenyl derivative of 1,2-dihydro-1-methyl-2-oxoquinoxaline to the corresponding *p*-aminophenyl compound.



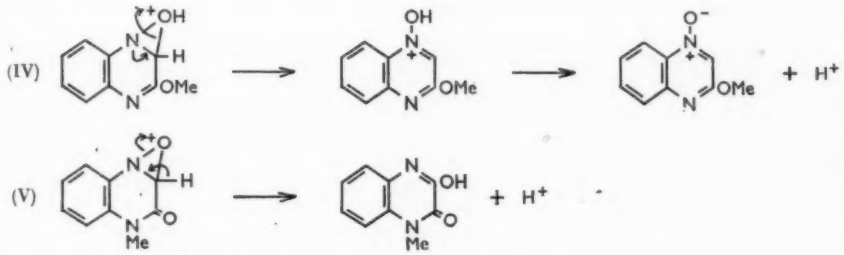
When a solution 1,2-dihydro-1-methyl-2-oxoquinoxaline in concentrated sulphuric acid was treated with potassium nitrate, 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (III) was obtained: under these conditions the base (pK_a −1·15) [1] will be predominantly in a protonated form. The structure of the nitration product was confirmed by synthesis from 2-methylamino-5-nitroaniline and butyl glyoxylate. The nitration of 2-hydroxyquinoxaline under similar conditions gave 2-hydroxy-6-nitroquinoxaline. This was converted into 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline by treatment with methyl iodide and methanolic sodium methoxide. Attempts to obtain this compound by methylation with methyl sulphate and alkali were not successful; reaction of the hydroxyquinoxaline with ethereal diazomethane gave the expected mixture [2] of *O*-methyl derivative (2-methoxy-6-nitroquinoxaline) and *CN*-dimethyl derivative (1,2-dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline). This dimethylnitroquinoxaline was also obtained on nitration of 1,2-dihydro-1,3-dimethyl-2-oxoquinoxaline; it was prepared previously by condensation of 2-methylamino-5-nitroaniline and pyruvic acid [3] and also by methylation of 2-hydroxy-3-methyl-6-nitroquinoxaline, the major nitration product of 2-hydroxy-3-methylquinoxaline in sulphuric acid.[4]

A recent report [5] that 2-hydroxyquinoxaline undergoes nitration in acetic acid at

[1] Part IV, Cheeseman, *J.*, 1958, 108.
[2] Cheeseman, *J.*, 1955, 3308.
[3] Kehrmann and Messinger, *J. prakt. Chem.*, 1892 (2), **46**, 573.
[4] Otomasa and Nakajima, *Chem. Pharm. Bull.* (*Tokyo*), 1958, **6**, 566; *Chem. Abs.*, 1959, **53**, 10,243.
[5] Kazuo Asano and Sotoo Asai, *Yakugaku Zasshi*, 1959, **79**, 567; *Chem. Abs.*, 1959, **53**, 21,979.

position 7 has been confirmed. Thus treatment of 2-hydroxyquinoxaline in acetic acid with one equivalent of fuming nitric acid gave 2-hydroxy-7-nitroquinoxaline. 2,3-Dihydroxy-6-nitroquinoxaline was a product of reaction when a ten-fold excess of nitric acid was used. The ready nitration of 2-hydroxyquinoxaline and related 1,2-dihydro-2-oxoquinoxalines is due to the cyclic NR·CO grouping (R = H or Me) and is in marked contrast with the resistance of quinoxaline itself to nitration: quinoxaline is said to resist nitration with fuming nitric and concentrated sulphuric acid at 100°,[5] and is converted [6] into a mixture of 5-nitro- and 5,6-dinitro-quinoxaline only after prolonged treatment with a mixture of fuming nitric and sulphuric acid at 90°. The nitration of other hydroxy-mono- and -di-azanaphthalenes leads to substitution at positions 3, 6, or 8 according to the conditions used,[7] and 2- and 4-hydroxypyridine both undergo ready electrophilic substitution at positions 3 and 5.[8] In 2-hydroxyquinoxaline, position 3 is deactivated by the adjacent ring-nitrogen atom. This nitrogen functions as the basic centre in the molecule, and clearly conjugate-acid formation will still further deactivate position 3 to electrophilic substitution. 2-Hydroxyquinoxaline is a very weak base (pK_a −1·4) [1] and so the different course of nitration in acetic and sulphuric acid may indicate that the principal species undergoing nitration in acetic acid is the free base and in sulphuric acid is the conjugate acid.

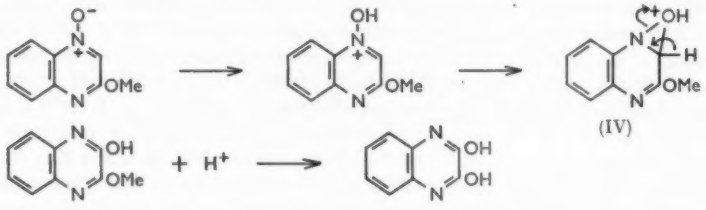
2-Hydroxy-6-nitroquinoxaline was readily converted into 2-chloro-6-nitroquinoxaline, and the 7-nitro-isomer into 2-chloro-7-nitroquinoxaline. Previous attempts to separate 2-chloro-6-nitroquinoxaline from mixtures of the two chloronitroquinoxalines have failed.[9,10,11] A mixture of 2-chloro-6- and -7-nitroquinoxaline, prepared by condensation of 4-nitro-1,2-phenylenediamine and butyl glyoxylate and subsequent chlorination,[9] has now been separated into the two pure chloronitroquinoxalines, and in this way confirmatory evidence for the structures of the corresponding hydroxynitroquinoxalines has been obtained.



Whereas oxidation of 1,2-dihydro-1-methyl-2-oxoquinoxaline with hydrogen peroxide and acetic acid gave 1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline in high yield, similar oxidation of 2-methoxyquinoxaline furnished mainly the 4-oxide. Under these conditions *N*-oxide formation may involve co-ordination of OH^+ with a ring nitrogen followed by elimination of a proton. Alternatively a cyclic intermediate of the type (IV) may be postulated. If, in the oxidation of 1,2-dihydro-1-methyl-2-oxoquinoxaline, a similar cyclic intermediate (V) is involved, hydroxylation subsequently requires the elimination, as a proton, of hydrogen linked to $C_{(3)}$. In *N*-oxide formation, it is the hydrogen linked to oxygen which is eliminated. The course of reaction may depend on the basicity of the ring-nitrogen atom involved: thus 2-methoxyquinoxaline (pK_a 0·28) [1] is a much

[6] Dewar and Maitlis, *J.*, 1957, 2518.
[7] Schofield, *Quart. Rev.*, 1950, **4**, 382.
[8] Albert, *J.*, 1960, 1020.
[9] Atkinson, Brown, and Simpson, *J.*, 1956, 26.
[10] Wolf, Pfister, Beutel, Wilson, Robinson, and Stevens, *J. Amer. Chem. Soc.*, 1949, **71**, 6.
[11] Horner, Schwenk, and Junghanns, *Annalen*, 1953, **579**, 212.

stronger base than 1,2-dihydro-1-methyl-2-oxoquinoxaline (pK_a −1·15).[1] 2-Methoxyquinoxaline 4-oxide and 2-ethoxyquinoxaline 4-oxide [12] rearrange under the influence of mineral acid into 2,3-dihydroxyquinoxaline and intermediates such as (IV) may be involved. Oxidation of 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline with hydrogen



(IV)

peroxide and acetic acid similarly gave 1,2-dihydro-3-hydroxy-1-methyl-6-nitro-2-oxoquinoxaline. This compound was also prepared by condensation of 2-methylamino-5-nitroaniline and ethyl oxalate.

2-Hydroxyquinoxaline underwent base-catalysed addition to acrylonitrile. Presumably a *N*-cyanoethyl derivative was formed and this was hydrolysed readily by aqueous alkali to the parent quinoxaline.

In conclusion it may be noted that 1,2-dihydro-2-oxoquinoxalines appear to undergo electrophilic attack either at position 4 (H^+ or OH^+) or at positions 6 or 7 (NO_2^+). Nucleophilic attack, as exemplified by methylation with diazomethane ($CH_2^-{\cdot}N^+{\equiv}N$), occurs at position 3. Further substitution reactions of these compounds are being studied.

Experimental

1,2-*Dihydro*-1-*methyl*-2-*oxo*-3-*phenylquinoxaline*.—(*a*) An aqueous solution of benzenediazonium chloride (20 ml.; from 1·5 ml. of aniline) was added at 5° to a stirred solution of 1,2-dihydro-1-methyl-2-oxoquinoxaline (2·66 g.) in water (125 ml.). The mixture was stirred and kept at 5° for 4 hr., set aside at 0° for a further 7 days, and then distilled in steam until the distillate no longer contained phenol. The residual solution was cooled to 0° and the precipitate (0·64 g.) then filtered off and crystallised twice from 96% ethanol. This gave 1,2-*dihydro*-1-*methyl*-2-*oxo*-3-*phenylquinoxaline*, m. p. 138—139°, not depressed on admixture with an authentic sample prepared as described below (Found: C, 75·9; H, 5·0; N, 12·2. $C_{15}H_{12}N_2O$ requires C, 76·25; H, 5·1; N, 11·9%). The initial aqueous filtrate was neutralised with sodium acetate and then extracted with chloroform. Evaporation of the dried (Na_2SO_4) extracts gave unchanged 1,2-dihydro-1-methyl-2-oxoquinoxaline (1·5 g.), m. p. 113—119°.

(*b*) A solution of freshly distilled *N*-methyl-*o*-phenylenediamine (2·6 g.) in 2N-sulphuric acid (35 ml.) was added to an aqueous solution of phenylglyoxylic acid (0·025 mole) and the mixture set aside at room temperature for 3 hr. The precipitate was then filtered off and washed with water. Crystallisation from 96% ethanol (70 ml.) gave 1,2-dihydro-1-methyl-2-oxo-3-phenylquinoxaline (3·49 g., 69%) as pale yellow needles, m. p. 138—139°.

(*c*) A solution of 2-hydroxy-3-phenylquinoxaline [13] (2·22 g., 0·01 mole) in 2N-sodium hydroxide (20 ml.) and water (80 ml.) was shaken with methyl sulphate (2·52 g., 0·02 mole) for 30 min. The precipitate was then filtered off and washed with water. Crystallisation from 96% ethanol gave 1,2-dihydro-1-methyl-2-oxo-3-phenylquinoxaline (1·8 g., 76%), m. p. 138—139°.

***Reaction of* 1,2-*Dihydro*-1-*methyl*-2-*oxoquinoxaline* *and* p-*Nitrobenzenediazonium Chloride*.**—An aqueous solution of *p*-nitrobenzenediazonium chloride (85 ml.; from 2·8 g. of *p*-nitroaniline) was added at 5° to a stirred solution of 1,2-dihydro-1-methyl-2-oxoquinoxaline (1·6 g.) in water (75 ml.). The mixture was set aside at room temperature for 36 hr., and the precipitate (2·55 g.)

[12] Newbold and Spring, *J.*, 1948, 519.
[13] Burton and Shoppee, *J.*, 1937, 546.

then filtered off. A second crop (0·15 g.) was collected after a further 72 hr. Crystallisation of the crude product from glacial acetic acid and then from benzene (65 parts) gave the p-*nitrophenyl derivative*, m. p. 247—248°, of 1,2-dihydro-1-methyl-2-oxoquinoxaline (Found: C, 64·4; H, 3·95; N, 14·8. $C_{15}H_{11}N_3O_3$ requires C, 64·0; H, 3·9; N, 14·9%).

Reduction of the p-*Nitrophenyl Derivative of* 1,2-*Dihydro*-1-*methyl*-2-*oxoquinoxaline*.—A suspension of the nitro-compound (1·4 g.) in concentrated hydrochloric acid (20 ml.) was stirred with a solution of stannous chloride dihydrate (6·8 g.) in concentrated hydrochloric acid (7 ml.) for 1 hr. The solid dissolved and then a crystalline complex separated. This was filtered off, suspended in boiling 0·2N-hydrochloric acid (50 ml.), and treated with hydrogen sulphide until no further precipitation of tin sulphide occurred. The hot mixture was filtered, and the filtrate freed from excess of hydrogen sulphide and then made alkaline. After cooling, the yellow precipitate (0·5 g.) was collected. Crystallisation from 96% ethanol (15 ml.) gave the p-*aminophenyl derivative* (0·42 g.), m. p. 156—157°, of 1,2-dihydro-1-methyl-2-oxoquinoxaline. The m. p. was raised to 158—159° by further crystallisation from 96% ethanol (Found: C, 71·9; H, 5·0; N, 16·6. $C_{15}H_{13}N_3O$ requires C, 71·7; H, 5·2; N, 16·7%).

1,2-*Dihydro*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline*.—(*a*) Powdered potassium nitrate (2·0 g., 0·02 mole) was added rapidly at 0° to a stirred solution of 1,2-dihydro-1-methyl-2-oxoquinoxaline (3·2 g., 0·02 mole) in concentrated sulphuric acid (20 ml.). The mixture was stirred at 0° for 30 min. and at room temperature for 2 hr., then slowly poured on crushed ice (*ca.* 500 ml.). The precipitate was filtered off and washed with water. Crystallisation from 96% ethanol (400 ml.) gave 1,2-*dihydro*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline* (3·3 g., 80%), m. p. 216—218°. The m. p. was raised to 219—220° by further crystallisation from 96% alcohol (120 parts) and was undepressed on admixture with an authentic sample prepared as described below (Found: C, 52·9; H, 3·7; N, 20·4. $C_9H_7N_3O_3$ requires C, 52·7; H, 3·4; N, 20·5%).

(*b*) A mixture of 2-methylamino-5-nitroaniline hydrochloride [14] (3·5 g.), butyl glyoxylate (2·86 g.), and N-hydrochloric acid (100 ml.) was shaken at room temperature for 1 hr. The precipitate was filtered off and extracted with boiling water (400 ml.). Insoluble material (1·3 g.) was removed and the extract was treated with charcoal, and then cooled. Yellow needles (1·0 g.) separated which, on crystallisation from 96% ethanol (80 ml.), gave 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (0·5 g.), m. p. 213—214°. The m. p. was raised to 219—220° by further crystallisation from 96% ethanol.

Nitration of 2-*Hydroxyquinoxaline*.—(a) *In sulphuric acid*. 2-Hydroxyquinoxaline (4·38 g., 0·03 mole) in concentrated sulphuric acid (50 ml.) was caused to react with potassium nitrate (3·0 g., 0·03 mole) similarly to 1,2-dihydro-1-methyl-2-oxoquinoxaline above. Crystallisation of the product from glacial acetic acid (200 ml.) gave 2-*hydroxy*-6-*nitroquinoxaline* (4·75 g., 83%), m. p. 298—302°. The analytical specimen was sublimed at 250°/1·0 mm. and crystallised from glacial acetic acid (60 parts); it had m. p. 300—302° (Found: C, 50·2; H, 2·4; N, 22·1. Calc. for $C_8H_5N_3O_3$: C, 50·3; H, 2·6; N, 22·0%). Horner, Schwenk, and Junghanns [11] give m. p. 294°.

(b) *In acetic acid*. Fuming nitric acid (0·88 ml., 0·02 mole) in glacial acetic acid (5 ml.) was added dropwise to a stirred solution of 2-hydroxyquinoxaline (2·92 g., 0·02 mole) in glacial acetic acid (85 ml.) at 18—20°. The mixture was left at room temperature overnight, then evaporated in a vacuum. Water was added to the residue and the pH adjusted to 5. The precipitate (3·3 g.) was filtered off, dried, and dissolved in acetone (450 ml.). 2-Hydroxy-7-nitroquinoxaline (1·1 g.), m. p. (mainly) 272—274°, separated from the cooled solution. Concentration of the mother-liquor yielded a further 0·6 g., m. p. (mainly) 268—274° (total yield, 45%). The analytical specimen was sublimed at 200°/0·1 mm. and crystallised from nitromethane (15 parts); it had m. p. 274—276° (Found: C, 50·4; H, 2·8; N, 22·0%). Atkinson, Brown, and Simpson [9] give m. p. 275—276°. 2,3-Dihydroxy-6-nitroquinoxaline was isolated from an experiment in which fuming nitric acid was used in ten-fold excess, and the reaction mixture was poured into water after 2 hr. It was characterised by conversion into 2,3-dichloro-6-nitroquinoxaline,[15] m. p. and mixed m. p. 152—153°.

Methylation of 2-*Hydroxy*-6-*nitroquinoxaline*.—(a) *With methyl iodide*. The hydroxyquinoxaline (1·4 g.) was dissolved in a solution of sodium methoxide (prepared from 0·23 g. of sodium and 50 ml. of methanol). Methyl iodide (0·62 ml.) was added and the mixture heated

[14] Pesin, Khaletskiĭ, and Chi-Chun Chao, *Zhur. obshchei Khim.*, 1957, **27**, 1570; *Chem. Abs.*, 1958, **52**, 3790.

[15] Curd, Davey, and Stacey, *J.*, 1949, 1271.

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under reflux for 2 hr. After cooling, the precipitate of 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (1·1 g.), m. p. and mixed m. p. 214—216°, was filtered off.

(b) *With diazomethane.* Ethereal diazomethane (from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide, 21·5 g.) was added to a stirred, ice-cooled suspension of the hydroxyquinoxaline (1·9 g.) in dry methanol (20 ml.). The mixture was stirred at 0° for 4 hr., and then left overnight at 0°. The precipitate (0·95 g.) was filtered off. Crystallisation (charcoal) from 96% ethanol and then from acetone gave 1,2-dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline, m. p. 219—222°, undepressed on admixture with an authentic specimen prepared as described below. The initial filtrate was evaporated in a vacuum. Crystallisation of the residue from light petroleum (b. p. 60—80°) and then benzene gave 2-*methoxy*-6-*nitroquinoxaline*, m. p. 169—170°, undepressed on admixture with a sample prepared as described below.

1,2-*Dihydro*-1,3-*dimethyl*-6-*nitro*-2-*oxoquinoxaline.*—(*a*) 1,2-Dihydro-1,3-dimethyl-2-oxoquinoxaline (5·22 g., 0·03 mole) in concentrated sulphuric acid (30 ml.) was caused to react with potassium nitrate (3·0 g., 0·03 mole) similarly to 1,2-dihydro-1-methyl-2-oxoquinoxaline above. Crystallisation (charcoal) of the product from acetone (350 ml.) gave 1,2-dihydro-1,3-dimethyl-6-nitro-2-quinoxaline (5·5 g., 84%), m. p. 220—223°. The m. p. was raised to 222—223° by crystallisation from 96% alcohol (200 parts) and undepressed on admixture with an authentic specimen prepared as described below (Found: C, 54·4; H, 4·2; N, 19·3. Calc. for $C_{10}H_9N_3O_3$: C, 54·8; H, 4·1; N, 19·2%).

(*b*) Pyruvic acid (1 ml.) was added to a solution of 2-methylamino-5-nitroaniline hydrochloride (1·75 g.) in N-hydrochloric acid (100 ml.). After 18 hr., the precipitate (0·6 g.; m. p. 218—220°) was filtered off and dried. Crystallisation from 96% alcohol (100 ml.) gave 1,2-dihydro-1,3-dimethyl-6-nitro-2-oxoquinoxaline, m. p. 222—223°.

2-*Chloro*-7-*nitroquinoxaline.*—A mixture of 2-hydroxy-7-nitroquinoxaline (0·8 g.), freshly distilled phosphoryl chloride (8 ml.), and phosphorus pentachloride (1·6 g.) was heated under reflux for 2 hr., then cooled and slowly poured into stirred ice-water. The precipitated 2-chloro-7-nitroquinoxaline (0·8 g.), m. p. 187—189°, was filtered off washed with sodium hydrogen carbonate solution and water, and then dried in a vacuum-desiccator over potassium hydroxide and phosphorus pentoxide. The m. p. was raised to 188—190° by crystallisation from benzene. Atkinson, Brown, and Simpson [9] give m. p. 185—186°.

2-*Chloro*-6-*nitroquinoxaline.*—(*a*) 2-Hydroxy-6-nitroquinoxaline (3·0 g.) was caused to react with phosphoryl chloride (30 ml.) and phosphorus pentachloride (6·0 g.) similarly to 2-hydroxy-7-nitroquinoxaline, above. The product (3·1 g., 94%), m. p. 208—209°, crystallised from benzene (20 parts) as pale yellow needles of unchanged m. p. (Found: C, 45·8; H, 2·3; N, 20·1; Cl, 16·95. Calc. for $C_8H_4ClN_3O_2$: C, 45·8; H, 1·9; N, 20·0; Cl, 16·9%). Horner, Schwenk, and Junghanns [11] give m. p. 202°.

(*b*) A mixture (6·25 g.) of 2-chloro-6- and -7-nitroquinoxaline (prepared by Atkinson, Brown, and Simpson's method [9]) was crystallised twice from benzene and then twice from 96% alcohol, and a fraction (0·90 g.), m. p. (mainly) 203—205°, thus obtained. The m. p. was raised to 208—209° by crystallisation from 96% alcohol (20 parts) and was undepressed on admixture with 2-chloro-6-nitroquinoxaline prepared as described above. Evaporation of the benzene mother-liquor gave a fraction (3·5 g.), m. p. (mainly) 163—165°. A portion (0·5 g.) was dissolved in benzene (20 ml.) and filtered through a column of aluminium oxide (100 g.; Spence, type H; mesh 100—200) prepared in benzene. Elution with benzene gave successively 2-chloro-7-nitroquinoxaline (0·23 g.; m. p. 187—188°), mixed solid of m. p. *ca.* 163—165°, and 2-chloro-6-nitroquinoxaline (0·02 g.; m. p. 202—204°). The analytical specimen of 2-chloro-7-nitroquinoxaline was crystallised from cyclohexane (150 parts) and had m. p. 188—190° (Found: N, 20·4; Cl, 17·35%).

2-*Methoxy*-6-*nitroquinoxaline.*—2-Chloro-6-nitroquinoxaline (1·05 g., 0·005 mole) was added to a solution of sodium methoxide prepared from sodium (0·23 g., 0·01 g.-atom) and methanol (20 ml.). The mixture was heated under reflux for 3 hr., then evaporated in a vacuum. Water was added to the residue, and the precipitate of 2-methoxy-6-nitroquinoxaline (0·95 g., 92%; m. p. 170—171°) was filtered off. Crystallisation from benzene (10 parts) gave pale yellow needles, m. p. 171—172° (Found: C, 52·3; H, 3·7; N, 20·2. $C_9H_7N_3O_3$ requires C, 52·7; H, 3·4; N, 20·5%).

1,2-*Dihydro*-3-*hydroxy*-1-*methyl*-2-*oxoquinoxaline.*—(*a*) A mixture of 1,2-dihydro-1-methyl-2-oxoquinoxaline (8·0 g., 0·05 mole), glacial acetic acid (100 ml.), and hydrogen peroxide (30% w/v; 50 ml.) was set aside at room temperature for 7 days. The crystalline precipitate of

1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline (7·15 g., 81%), m. p. 285—286°, was then filtered off, washed with water, and dried at 100°.

(*b*) Methyl sulphate (120 ml.) was added dropwise to a stirred solution of 2,3-dihydroxyquinoxaline (48·6 g.) in 2N-sodium hydroxide (1200 ml.). The mixture was stirred for a further 2 hr., and the precipitate was then filtered off and triturated with excess of 2N-acetic acid. Filtration gave 1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline (27·0 g., 51%), m. p. (mainly) 279—281°. The m. p. was raised to 285—286° by crystallisation from glacial acetic acid (6 parts). The initial aqueous filtrate was extracted with chloroform, and the combined extracts were washed with water, dried (Na_2SO_4) and evaporated. Crystallisation of the residue (13·0 g.) from ethanol (600 ml.) gave 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (10·3 g., 18%), m. p. 252—253°.

2-*Methoxyquinoxaline* 4-*Oxide*.—A mixture of 2-methoxyquinoxaline (4·8 g., 0·03 mole), glacial acetic acid (60 ml.), and hydrogen peroxide (30% w/v; 30 ml.) was heated at 55° for 14 hr., and then concentrated to small bulk in a vacuum. Water (15 ml.) was added and, after cooling to 0°, the product (3·5 g.) was filtered off. Crystallisation from methanol–N-sodium hydroxide (1 : 1; 35 ml.) gave 2-methoxyquinoxaline 4-oxide (1·83 g., 35%) as needles, m. p. 105—108°. The m. p. was raised to 106—108° by crystallisation from aqueous methanol (Found: C, 61·1; H, 4·65; N, 16·2. $C_9H_8N_2O_2$ requires C, 61·35; H, 4·6; N, 15·9%).

A mixture of 2-methoxyquinoxaline 4-oxide (0·36 g.), ethanol (3 ml.), and 2N-hydrochloric acid (3 ml.) was heated under reflux for 3½ hr. and then evaporated to dryness. The residue was extracted with 2N-sodium hydroxide, and insoluble matter filtered off. Acidification of the filtrate with acetic acid gave 2,3-dihydroxyquinoxaline (0·26 g.). This was identified by conversion [2] into 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline, m. p. and mixed m. p. 252—253°.

1,2-*Dihydro*-3-*hydroxy*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline*.—(*a*) A mixture of 1,2-dihydro-1-methyl-6-nitro-2-oxoquinoxaline (1·0 g., 0·005 mole), glacial acetic acid (45 ml.), and hydrogen peroxide (30% w/v; 5 ml.) was set aside at room temperature for 7 days. The crystalline product (0·85 g.) was then filtered off. Crystallisation from glacial acetic acid (85 ml.) gave 1,2-*dihydro*-3-*hydroxy*-1-*methyl*-6-*nitro*-2-*oxoquinoxaline* (0·6 g.), m. p. 350—352° (decomp.), not depressed on admixture with an authentic sample prepared as described below (Found: C, 49·0; H, 2·9; N, 18·6. $C_9H_7N_3O_4$ requires C, 48·9; H, 3·2; N, 19·0%).

(*b*) A mixture of 2-methylamino-5-nitroaniline (0·5 g.) and ethyl oxalate (5 ml.) was heated under reflux for 15 min., and then cooled. The precipitate (0·47 g.) was filtered off and washed with 96% alcohol. Crystallisation from glacial acid gave 1,2-dihydro-3-hydroxy-1-methyl-6-nitroquinoxaline (0·41 g.), m. p. 350—352° (decomp.).

Reaction of 2-*Hydroxyquinoxaline and Acrylonitrile*.—A solution of 2-hydroxyquinoxaline (7·3 g.), acrylonitrile (10 ml.), and 15N-sodium hydroxide (12 drops) in 96% ethanol (250 ml.) was heated under reflux for 20 hr., then concentrated to *ca.* 50 ml. After cooling to 0°, the crystalline precipitate was filtered off and triturated with 2N-sodium hydroxide (25 ml.). Filtration gave the (?1-)*cyanoethyl*-1,2-*dihydro*-2-*oxoquinoxaline* (5·4 g., 54%), m. p. (mainly) 203—208°. The m. p. was raised to 207—208° by crystallisation (charcoal) from 96% ethanol (220 ml.) (Found: C, 66·5; H, 4·4; N, 21·3. $C_{11}H_9N_3O$ requires C, 66·3; H, 4·5; N, 21·1%).

The cyano-compound (2·0 g.) and 2N-sodium hydroxide (20 ml.) were heated under reflux for 25 min., and then in an open flask for 5 min. to expel most of the ammonia. The mixture was acidified with 2N-acetic acid, and after cooling, the precipitate of 2-hydroxyquinoxaline (1·5 g.), m. p. (mainly) 263—265°, was filtered off.

The author is grateful to Professor H. Burton for his encouragement and to Mrs. Muriel Phillips and Mr. Anthony Sarsfield for technical assistance.

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[*Received, June 21st,* 1960.]

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244. *The Production of Active Solids by Thermal Decomposition. Part XIII.*[1] *The Calcination of Ion-free Hydrous Titania.*

By S. J. Gregg and M. I. Pope.

Two batches of hydrous titania have been prepared by hydrolysis of n-butyl titanate, one contaminated with vanadium ions but the other virtually free from foreign metal ions. Separate portions of each batch were calcined for five hours, at a succession of temperatures, and the following properties of the cooled product were determined: the specific surface by the sorption of nitrogen, the pore volume by the sorption of benzene, and the percentage of rutile and of anatase by *X*-ray examination. In both batches an accelerated rate of sintering (as indicated by loss of surface area and of pore volume) and the inception of the phase change from anatase to rutile both occur at about 650° which is probably close to the Tammann termperature of titania. This behaviour contrasts with that of the titania of Part XII (contaminated with sulphate ions) where an acceleration in sintering still occurred at the Tammann temperature but the phase change did not start till about 1050°.

In Part XII [1] the effect of heat on the activity of hydrous titania was reported. The starting material, which simulated the hydrous titania used in the industrial preparation of titania pigments, contained an appreciable percentage of ionic impurities. In view of the known effect of such impurities both on sintering behaviour and on the temperatures at which the transformation from the anatase to rutile occurs, a similar investigation has been made with a virtually ion-free titania made by hydrolysis of an alkyl titanate.

Results show that, whereas at temperatures below the Tammann region the sintering behaviour is only slightly different whether foreign ions are absent or present, yet in the absence of ions both the inception of the phase change and an acceleration of sintering—as measured by the fall in specific surface and in pore volume—take place in the region of the Tammann temperature.

Experimental

Materials.—Two batches of hydrous titania were prepared, the first (A) being used for some preliminary experiments, and the second (B) for the main study. Batch A was prepared from a sample of n-butyl titanate (containing 0·2% of vanadium) which was purified by distillation under 4 mm. pressure, the fraction boiling at 146° being collected. A 50% solution of the distillate in n-butyl alcohol was then hydrolysed by running it dropwise into a 5% solution of water in ethyl alcohol under nitrogen, with stirring. The gel-like precipitate was separated by decantation and washed with a large excess of distilled water; it had a pale cream colour (attributable to vanadium ions), but neither iron nor butyl alcohol was present in detectable quantities.

Batch B was prepared from a specimen of specially purified n-butyl titanate (Laporte Titanium Ltd.), containing less than 10 p.p.m. of vanadium, the main metallic impurity. It was hydrolysed by being added dropwise to distilled water, precautions being taken to avoid change in pH by atmospheric contamination: the water had been boiled out and cooled under nitrogen, and it was mechanically stirred in an atmosphere of nitrogen whilst the alkoxide was being added. The white gelatinous precipitate was separated by decantation and air-dried at 25°.

A " calcination series " was then prepared from each batch of hydrous titania: separate samples were heated in a silica crucible at a series of fixed temperatures (T) in a vertical electric furnace ($\pm 4°$), the furnace being raised to T during 30 min. and kept there for 5 hr.; the crucible was then removed and allowed to cool in air.

The following properties of the calcined samples were examined: (1) specific surface by nitrogen adsorption at −183°, (2) phase composition and crystallite size by *X*-ray analysis,

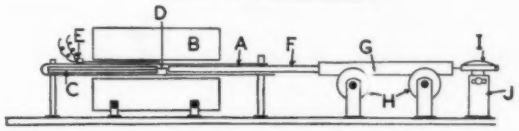
[1] Part XII, Asher and Gregg, *J.*, 1960, 5057.

(3) pore structure by benzene sorption isotherms at 25°, and (4) electron micrographs. In addition, a sample of the starting material of each batch, made into a pellet under pressure, was subjected to a steadily rising temperature, and its length measured at frequent intervals in an extensometer.

The measurements of the sorption of nitrogen at −183°, and of benzene at 25°, were carried out gravimetrically on an electromagnetic sorption balance,[2] housed, together with the arrangements for storing and manipulating the adsorbate, in an air thermostat kept at 25°; the sample (1—2 g.) was outgassed at 100° until the fractional rate of loss in weight fell to less than 0·1% per hour.

The proportions of anatase and of rutile were determined by means of an automatically recording *X*-ray diffraction apparatus described by Richmond and Watson,[3] which gave direct readings of the percentages of the two forms. A modification of the apparatus permitted the broadening of the *X*-ray diffraction lines to be determined, and hence the mean apparent crystallite sizes of the samples to be estimated.

FIG. 1.—*The extensometer.*



For the extensometric examination, the air-dried material, in powder form, was compressed at 32,000 lb. in.$^{-2}$ in a die $\frac{3}{8}''$ in diameter, for 5 min., to give a pellet 20—30 mm. long. The pellet was subjected to a temperature rising at 200° per hr. in an extensometer (Fig. 1) consisting of a Mullite tube *A* (15 mm. internal diameter) closed at one end and mounted horizontally in a tubular electric furnace (*B*). A fluted silica spacer (*C*) kept the compact sample (*D*) in a fixed position near the centre of the furnace and directly below the junction of a platinum–rhodium thermocouple (*E*). The Mullite rod (*F*), 12 mm. in diameter, had one end inserted concentrically into a silver-steel rod (*G*) balanced so as to move freely on two low-friction pulley wheels (*H*). The rod (*F*) was pressed against the pellet by the spring-loaded probe of the dial indicator gauge (*I*), which was bolted securely in position on the slotted bracket (*J*) with the probe fully depressed against the steel rod (*G*). In this way changes in length of as little as 0·002 mm. can be measured with a total range of 13 mm. Corrections were made for the slight lag in the temperature of the sample from that of the furnace.

RESULTS AND DISCUSSION

We now compare the results from the two batches with those for the titania (hereafter called batch XII) described in Part XII.[1] Below 600° the plots of specific surface against temperature are broadly similar for all three batches (Fig. 2), the maximum in the curve for batch A being explained in terms of the removal of water from previously blocked pores in the manner suggested in Part XII. The absence of the maximum in the curve for batch B is probably attributable to the removal of such water during preparation and storage, for this material was air-dried at 27° and stored in a well-stoppered bottle, whereas batch A had been stored in a desiccator at a relative humidity of 50%. The loss of area with increasing temperature of calcination is the result of sintering. As in Part XII, any increase in specific surface *S* of the kind to be expected if chemical decomposition occurs is again absent, in accordance with the fact that titania is a hydrous oxide, so that no change in lattice structure occurs when water is expelled.[4]

Commencing at a temperature between 600° and 700°, say *ca.* 650°, the loss of area by sintering accelerates, as is again brought out by plotting log *S* against $1/T$ ($T°$ K is the temperature of calcination). For batch B (the ion-free material), indeed, the break

[2] Gregg, *J.*, 1955, 1438.
[3] Richmond and Watson, *J. Oil Colour Chemists Assoc.*, 1952, **35**, 162.
[4] Weiser and Milligan, *Chem. Rev.*, 1939, **25**, 1.

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in the curve (Fig. 3) is quite sharp if the point for 700° is ignored, and there can be little doubt that a new mechanism of sintering has come into operation at about 650°; and, as pointed out in Part XII, this temperature could well lie close to the Tammann temperature of titania. The curve for the total pore volume V (Fig. 4) for batch B (that for

FIG. 2. *Plot of specific surface, S (surface area in m.² g.⁻¹) (by sorption of nitrogen at −183°) against temperature of calcination for batches* (A (*dotted line*), B (*broken line*), *and* XII (*full line*). (*Inset: Enlarged high-temperature region of curve for batch* B.)

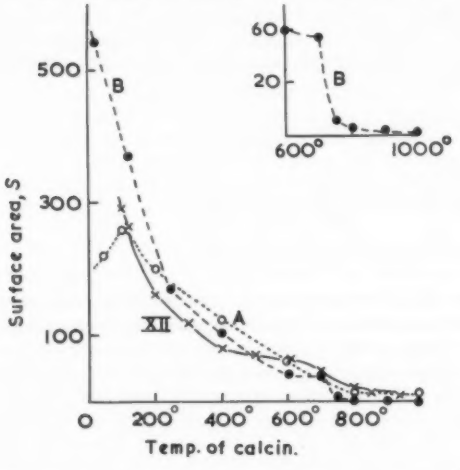


FIG. 3. *Plot of* $\log_{10} S$ (S = *surface area in m.² g.⁻¹*) *against the reciprocal of the temperature of calcination (in °K) for batches A and B.*

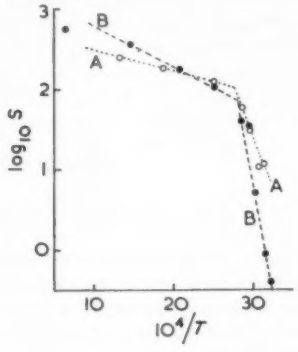


FIG. 4. *Plot of* $100(l_T - l_{1000})/l_{1000}$ *against temperature of calcination (where* l_T *is the length at temperature T) for pellets from batches A and B. Curve C illustrates the total pore volume (cm.³/g.) plotted against temperature of calcination for batch B.*

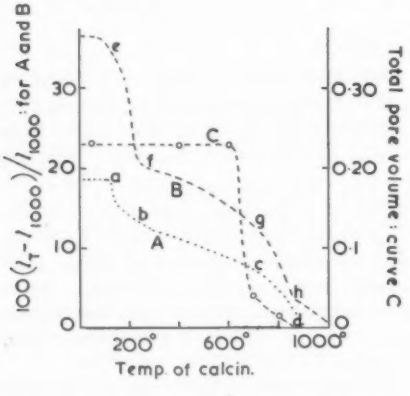
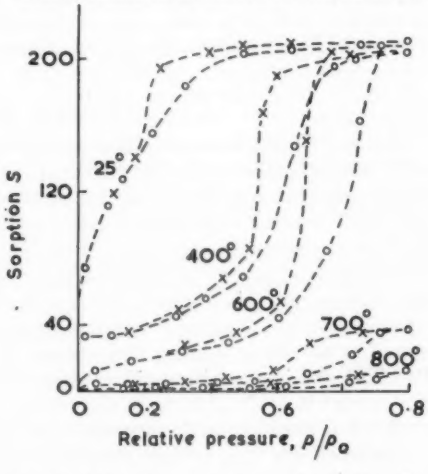


FIG. 5. *Sorption isotherms (mg./g.) of benzene at 25° on batch B (ion-free) titania. (The temperatuce of calcination is marked on each isotherm.)*



batch A was not measured) is also similar to that for batch XII, with the interesting difference that V remains sensibly constant to 600° and then falls, whereas with batch XII the curve was somewhat rounded off in the region 400—600°. The concept of a framework which undergoes progressive and fairly rapid collapse once the Tammann temperature

has been passed is again apposite, the onset of the collapse being sharper in the ion-free material of batch B than with the contaminated material of batch XII. The adsorption isotherms of benzene (Fig. 5) indicate that the pore-size distribution changes in favour of the larger pores at temperatures up to 600° even though the total pore volume is virtually unchanged, again in accordance with the framework model.

With batch XII the phase change of anatase to rutile commenced at about 950°, corresponding to $0{\cdot}58T_m$ (where T_m° K is the m. p. of rutile) and so is well above the Tammann range [5] ($0{\cdot}37$—$0{\cdot}52\ T_m$)—particularly if, as seems probable from the sintering results, the Tammann temperature is at 650°. In the case of batch B the phase change (Fig. 6) begins slightly below 600° and is almost complete in the 800° specimen; with batch A the change occurs over a somewhat wider range of temperature, the proportion of rutile being greater at the low-temperature end and somewhat smaller at the high-temperature end than with batch B. It thus seems that with both batches the inception of the phase change and an acceleration of sintering each occur at a temperature near to the Tammann temperature.

Electron micrographs furnished interesting confirmation of the accelerated sintering above 600°. They showed a marked increase in particle size between 600° and 750°,

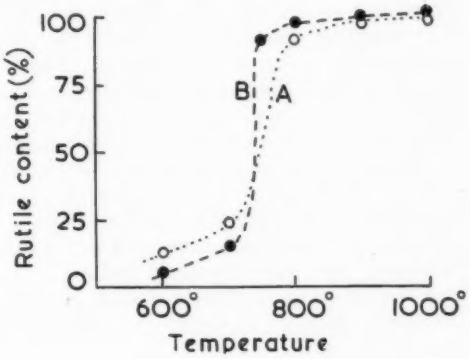


FIG. 6. *Plot of the percentage of rutile against temperature of calcination for batches A and B.*

and also the very rounded appearance of the particles and the paucity of very fine particles at 1000°. Other workers [6] have also noted that, on calcination of hydrous titania, growth in crystallite size commences at about 600°.

There is thus a significant difference between the behaviour of the batches A and B on the one hand and batch XII on the other, for in batch XII there was an acceleration of sintering at about 600° but the onset of the phase change was delayed till 950°. It thus seems that the impurities in batch XII did not noticeably shift the Tammann temperature but prevented the phase change at this temperature. Since the phase change would require, not only the mobility of the constituent ions, but also the formation of growth nuclei,[7] one infers that the impurities have inhibited the formation of such nuclei without adversely affecting the ionic mobility. This state of affairs does not seem unreasonable inasmuch as suitable impurities could promote the formation of defects and thus enhance ionic mobility, whereas the formation of nuclei could be hindered by the accumulation of impurities in positions, *e.g.*, along dislocation lines,[8] where nuclei might otherwise be formed.

The specific surface for 700° at first sight seems anomalously high (Fig. 2, inset, and

[5] Finch and Sinha, *Proc. Roy. Soc.*, 1957, *A*, **239**, 145.
[6] Sullivan and Cole, *J. Amer. Ceram. Soc.*, 1959, **42**, 127.
[7] Czanderna, Rao, and Honig, *Trans. Faraday Soc.*, 1958, **54**, 1069.
[8] Cottrell, "Dislocations and Plastic Flow in Crystals," Oxford Univ. Press, 1953.

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Fig. 3); but, as already pointed out,[9] an increase in area might well be expected when a phase change occurs, but it is opposed by the accelerated sintering, so that the areas actually registered along the curve result from the balance between the two processes. A high value at a particular temperature then merely implies that the loss of area by sintering was at that temperature less important relative to the gain of surface by activation than it was at neighbouring temperatures.

The extensometric data (Fig. 4) broadly support these interpretations. For each of the batches there is an increased rate of contraction commencing between 700° and 750°. To verify that this contraction accompanied the phase change from anatase to rutile, two pellets of batch B were subjected to the same rate of rise of temperature as in Fig. 4 and were removed from the furnace at a temperature corresponding to points "*g*" and "*h*" respectively; the rutile contents were found to be 2% and more than 98%, respectively, showing that the phase change occurs almost entirely between these two temperatures in batch B. The contractions *ab* and *ef* are caused largely by loss of adsorbed water, and *bc* and *fg* by sintering: with a steadily rising temperature any features are likely to be spread over a wider range of temperature and to be displaced towards the high-temperature side.

As will be noted, however, the volume of the pellet, unlike the pore volume, was diminishing steadily even at temperatures below the Tammann temperature, so that at no temperature was there evidence of the kind of stable framework which seemed to be present in the uncompressed samples. This is not altogether unexpected: the very high pressure used for compression would largely break up the framework and bring the particles within the grains into much closer contact; this would promote sintering by adhesion, which can occur at temperatures much below the Tamman temperature (cf. Part I [9]).

Finally, a comparison of the value of the crystallite size (l_s) calculated from the specific surface with that (l_x) calculated from the *X*-ray line broadening is interesting ($l_s = 6/S$, if particles are assumed to be isodimensional). l_x corresponds to regions of crystal perfection, whereas l_s merely measures the size of particles into which nitrogen molecules cannot penetrate; such particles could include several perfect crystallites, imperfectly aligned with respect to each other, any gaps between the crystallites being too small to admit nitrogen molecules. l_x should therefore never exceed l_s and, as is seen (Table), this is actually found.

Mean apparent crystallite sizes (in Å) of samples of batch B titania, calculated (1) *from X-ray line broadening and* (2) *from nitrogen adsorption at* −183°.

Temp. of calcin. ...	25°	250°	400°	600°	700°	750°	800°	900°	1000°
(1) l_x	—	—	92	134	269*	523	523	864	—
(2) l_s	27	91	146	385	417	2850	6400	12,700	35,300

* This figure refers to anatase; for rutile it is 393.

Conclusion.—In ion-free titania the phase change from anatase to rutile and accelerated sintering both commence at approximately 600°, close to the probable Tammann temperature of titania. Comparison with the results of Part XII suggests that the presence of certain impurities considerably raises the temperature at which the phase change commences without greatly influencing the temperature at which accelerated sintering (which in particular leads to a rapid reduction in pore volume) sets in.

Thanks are offered to Messrs. Laporte Titanium Ltd. for a maintenance grant (to M. I. P.) and for a grant towards the purchase of apparatus, to Mr. J. T. Richmond for his continued interest in this work, and to Mr. J. E. Latty for taking electron micrographs.

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THE UNIVERSITY, EXETER.

[*Received, July 25th*, 1960.]

[9] Gregg, *J.*, 1953, 3940.

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245. *Metal Chelates. Part II.* Phthalocyanine–Chromium Complexes and Perpendicular Conjugation.*

By J. A. Elvidge and A. B. P. Lever.

The phthalocyanine derivatives of chromium(II) and chromium(III) have been isolated and a number of octahedral derivatives—cationic, neutral, anionic complexes—have been prepared. Magnetic moments and light absorptions are recorded. These data and perpendicular conjugation are discussed.

Chromium derivatives of phthalocyanine have not before been properly authenticated.[1,2] We have now obtained pure both chromium(II) and chromium(III) phthalocyanine, the latter as hydroxide and acetate, and have made several 6-co-ordinate (octahedral) derivatives for the first time. Properties of the octahedral complexes suggest that the groups attached to the metal in the plane perpendicular to the aromatic phthalocyanine system (*i.e.*, in the fifth and the sixth co-ordination position) are conjugated to it. The feasibility of perpendicular conjugation (through a metal atom) was discussed by us in a preliminary communication.[3] Further comment is made below.

Tervalent Chromium Phthalocyanines.—(a) *Cationic complexes.* Interaction of chromium salts with phthalonitrile, *o*-cyanobenzamide, or 1,3-di-iminoisoindoline gave mixtures of chromic complexes together with chromous material, which could not be separated satisfactorily by chromatography or fractional crystallisation. The preferred, exothermic reaction of chromium(III) acetate with phthalonitrile at 270° afforded a product which contained phthalocyanine chromium(II) (II) and phthalocyanine chromium(III) acetate (I) from which some hydroxide (IV) was apparently formed during preliminary washing. When the washed product was heated at 400° under reduced pressure, the hydroxide and the chromium(II) complex sublimed, the latter with considerable oxidation, so that repeated sublimation at a low pressure of air afforded pure phthalocyanine chromium(III) hydroxide, PcCr·OH. This appeared as dark purple needles: its solution in, *e.g.*, chlorobenzene was green, like that of many other metal phthalocyanines. Support for the constitution (IV) came from quantitative oxidation, the magnetic moment (Table 1),

Table 1. *Magnetic moments at room temperature.*

Structure	Assumed metal-ligand bonding	No. of unpaired electrons	Theor. moment (B.M.)	Found $\mu_{eff.}$* (B.M.)	Found θ (°K)
PcCr (II)	dsp^2	4	4·90	3·49	−306
PcCr,2py (V)	d^2sp^2	2	2·83	3·16	−35
PcCr·OH (IV)	dsp^2	3	3·87	4·03	−15
PcCr(H_2O)·OH (VII)	d^2sp^2	3	3·87	3·69	0
$2Na^+[PcCr(OH)O]^{2-}$ (VIII; M = Na)	d^2sp^2	3	3·87	3·91	−155
$2pyH^+[PcCr(OH)O]^{2-}$ (VIII; M = C_5H_6N)	d^2sp^2	3	3·87	4·06	−15

* Calc. from $\mu_{eff.} = 2{\cdot}839(\chi'_m T)^{\frac{1}{2}}$.

similarity of the light absorption to that of established 4-co-ordinate metal phthalocyanines (Tables 2, 3), and the ready solvation of the cation by *two* molecules of, *e.g.*, water and methanol (see below). Treatment with cold acetic anhydride gave the acetate

* Part I, *J.*, 1961, 869.

[1] Barrett, Dent, and Linstead, *J.*, 1936, 1719.

[2] B.P. 457,526/1936; Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151; Bigelow and Perkins, "Chemistry of Synthetic Dyes and Pigments," A.C.S. Monograph No. 127, Reinhold Publ. Inc., New York, 1955, Chapter 9.

[3] Elvidge and Lever, *Proc. Chem. Soc.*, 1959, 123.

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PcCr·OAc, which appears better represented as a 6-co-ordinate lattice compound (I) than as the 4-co-ordinate ionic acetate corresponding to the hydroxide (IV). Reasons are that it is involatile even at 400° in a vacuum, it is highly insoluble (unlike the hydroxide), it

TABLE 2. *Infrared absorptions* (3—14 μ) *of phthalocyanines*, PcM, *in Nujol mull.*

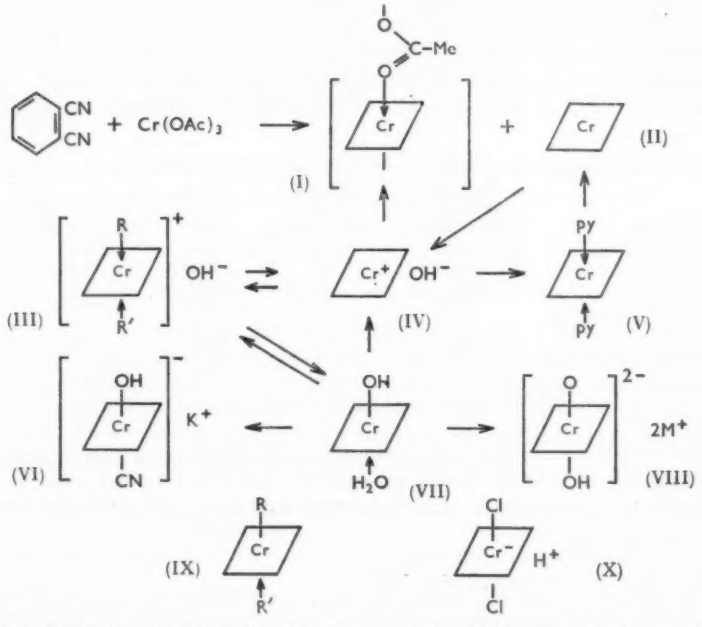
Common vibrations (cm.$^{-1}$) for all complexes listed below: 1609 ± 10 w—m, 1420 ± 10, 1333 ± 6 m—s, 1287 ± 4, 1164 ± 6, 1120 ± 4 s, 1085 ± 6 m—s, 1071 ± 8, 903 ± 13 m—s,* 779 ± 4 w—s, 755 ± 2 s, 726 ± 9 s.

* w, in $PcCr^{II}$,2py.

Additional (characteristic) vibrations:

$PcCr^{III}$·OH	1503w, 1035	$2Na^+[PcCr^{III}(O)OH]^{2-}$	1484w, 1051w
$PcCr^{III}$·OAc	1709, 1504w, 1486, 1000w, 769w	$K^+[PcCr^{III}(OH)CN]^-$	2137w, 1486, 956w, 695w
$PcCr^{III}(H_2O)_2$·OH	1565s, 1488, 1390w, 1079s, 1016	$2pyH^+[PcCr^{III}(O)OH]^{2-}$	2527w, 1715w, 1626, 1571w, 1486, 1343, 1301, 1220, 1153w, 1046w, 1012, 941w, 875w, 702
$PcCr^{III}(MeOH)_2$·OH	1505w, 1484w, 1032, 871, 783		
$PcCr^{III}(H_2O)$·OH	1568s, 1507w, 1486, 1390w, 1079s, 1016	$PcCr^{II}$,2py	1600w, 1485w, 1216w, 1150, 1043, 760, 629
$PcCr^{III}(H_2O)$·OAc	1715w, 1569s, 1487, 1015	$PcCo^{II}$ [a]	1515, 879, 774
$PcCr^{III}(H_2O)$·O·CO·Et	1715w, 1582w, 1487, 1188w, 951, 874w	$PcFe^{II}$ [a]	1505, 872, 769w
$PcCr^{III}(MeOH)$·OAc	1715w, 1543s, 1487, 1024	$PcFe^{II}$,2py [a]	1584w, 1501s, 1480w, 1211w, 1146w, 1112, 1100, 930w, 866w, 761w, 691
$PcCr^{III}(AcOH)$·OAc	1718w, 1493, 1403, 1164w, 1046, 1000		
$HPcCr^{III}Cl_2$	1514, 1502w, 1487, 1305w, 1219w, 1143w, 1096w, 952, 899, 739w, 705		

Whalley, *J.*, 1961, 866.



These rhombs represent square planar 4-co-ordinate bivalent phthalocyanine ligand, $C_{32}H_{16}N_8$.
py = pyridine.

shows carbonyl absorption at 1709 cm.$^{-1}$ (Table 2) which indicates that the acetate grouping is covalently linked, and it absorbs at 1486 cm.$^{-1}$, a frequency at or near which all the undoubted 6-co-ordinate complexes (described below) show a maximum.

The 4-co-ordinate cation of phthalocyanine chromium(III) hydroxide (IV) was readily solvated to the 6-co-ordinate state, and the products were unusual amongst phthalocyanines in being noticeably soluble in simple solvents such as methanol, ether, acetic acid. Boiling methanol afforded the dimethanol solvate (III; R = R′ = MeOH), warm aqueous methanolic acetic acid the aquo-methanolate (III; R = H_2O, R′ = MeOH), and aqueous ethanolic acetic acid the dihydrate (III; R = R′ = H_2O). The cationic nature of these phthalocyanine complexes was demonstrated by electrophoresis on paper.

These 6-co-ordinate cationic complexes were not thermally stable. At 180°/20 mm., the dimethanolate (III; R = R′ = MeOH) was desolvated to the starting material (IV), but the aquo-methanolate lost only methanol, and the dihydrate only a mol. of water, both yielding the compound PcCr·OH,H_2O. That this new product was still a tervalent chromium complex was shown by the magnetic moment (Table 1), so it seems best formulated as (VII), covalent 6-co-ordinate phthalocyanine hydroxoaquochromium(III). Only at 400° under a vacuum could it be dehydrated to yield, as sublimate, phthalocyaninechromium(III) hydroxide (IV). On the other hand, it combined readily with hot water to regenerate the dihydrated ionic hydroxide (III; R = R′ = H_2O), in this respect behaving as a base. The thermal conversion of the aquo-methanolate hydroxide (III; R = H_2O, R′ = MeOH) into the hydroxoaquo-complex (VII) is typical. Thus the complex salt $[Cr(NH_3)_5H_2O]^{3+}$ $3Cl^-$ is transformed[4] by heat into $[Cr(NH_3)_5Cl]^{2+}$ $2Cl^-$ and not into $[Cr(NH_3)_5OH]^{2+}$ $2Cl^-$, an anion substituting a co-ordinate position rather than abstracting a proton.

Mild treatment of the covalent hydroxoaquo-complex (VII) with acetic anhydride and with propionic anhydride gave respectively phthalocyanine acetatoaquochromium(III) (IX; R = OAc, R′ = H_2O) and the corresponding propionatoaquo-complex (IX; R = O·CO·Et, R′ = H_2O). The infrared absorptions (Table 2) of these complexes, and of others described below, confirmed the covalent bonding of the carboxylate residues. Boiling acetic anhydride converted the hydroxoaquo-complex (VII), and also phthalocyanine chromium(III) hydroxide (IV) into a complex containing two acetic residues. This may be formulated as (covalent) phthalocyanine acetato(acetic acid)chromium(III) (IX; R = OAc, R′ = HOAc). Each of the foregoing complexes (IX) was stable at 180°/20 mm. A less stable analogue, phthalocyanine acetatomethanolchromium(III) (IX; R = OAc, R′ = MeOH), was formed from phthalocyanine chromium(III) hydroxide (IV) and boiling methanolic acetic acid; at 180°/20 mm., the complex lost methanol to yield the previously encountered phthalocyanine chromium(III) acetate (I).

It seems possible in these conversions of phthalocyanine chromium(III) hydroxide (IV) into the covalent diacetate and acetato-methanolate, that the cation is first solvated to labile 6-co-ordinate species which then undergo anion attack (by OAc^-, here), analogously to the conversion of the aquo-methanolate (III; R = H_2O, R′ = MeOH) (and presumably the related diaquo-complex) into phthalocyanine hydroxoaquochromium(III) (VII).

When dry hydrogen chloride was passed into a boiling methanolic suspension of phthalocyanine chromium(III) hydroxide (IV), a dichloro-complex was formed. The stability of this at 180°/20 mm. and its infrared absorption (Table 2) suggested its formulation as the 6-co-ordinate hydrogen [phthalocyanine dichlorochromate(III)] (X), rather than as the hydrochloride of 4-co-ordinate phthalocyanine chromium(III) chloride. The dichloro-complex was readily hydrolysed by aqueous alcohol to hydrogen chloride and phthalocyanine diaquochromium(III) hydroxide (III; R = R′ = H_2O).

(b) *Anionic complexes.* The observation that phthalocyanine chromium(III) hydroxide (IV) and the covalent hydroxoaquo-complex (VII) dissolved appreciably in alcoholic

[4] Benrath, *Z. anorg. Chem.*, 1928, **177**, 286.

potassium cyanide led to the discovery of potassium [phthalocyanine hydroxocyanochromate(III)] (VI). This showed similar infrared absorption to other metal phthalocyanines but with an additional band at 2137 cm.$^{-1}$ (Table 2), which is close to the C≡N stretching at 2127 cm.$^{-1}$ in the hexacyanochromate(III) anion.[5] The visible-light absorption of a methanol solution of the monocyano-complex (VI) soon changed in the absence of cyanide ion, indicating hydrolysis. Addition of an excess of potassium cyanide, however, caused further changes in the light absorption (Table 3) suggestive of the formation of potassium [phthalocyanine dicyanochromate(III)]. Similar indications of the formation of thiocyanato- and selenocyanato-anionic complexes were obtained on dissolution of phthalocyanine chromium(III) hydroxide (IV) in methanolic potassium thiocyanate and selenocyanate; unfortunately, attempts to isolate these complexes failed.

It was also found that the slight solubility of the hydroxoaquo-complex (VII) in ethanol was much increased by addition of sodium hydroxide. Evidently the complex was acidic, and this was further indicated by electrophoresis of a drop of the alkaline solution on paper whereupon the coloured spot migrated towards the anode. That *two* protons were displaceable from the complex (VII) was indicated by the isolation of disodium [phthalocyanine oxohydroxochromate(III)] (VIII; M = Na). With liquid ammonia, the hydroxoaquo-complex (VII) gave a diammonium salt, but this was unstable at room temperature. Treatment of the complex (VII) with pyridine, however, gave a well-defined dipyridinium salt (VIII; M = C_5H_6N), the constitution of which was supported by the magnetic moment (Table 1), stability at 180°/15 mm., electrophoretic migration of the coloured ion towards the anode, and infrared absorption (Table 2).

Bivalent Chromium Phthalocyanines.—When treated with acid-free pyridine, phthalocyanine chromium(III) hydroxide (IV) underwent rapid reduction to phthalocyanine dipyridinechromium(II), PcCr py_2. This is a very dark green solid which gives rich blue solutions, in contrast to the dull green solutions of the starting material (IV). The bivalency of the metal in this dipyridine complex (V) was shown by quantitative oxidation, whilst the 6-co-ordinate nature of the complex, suggested by the thermal stability, was supported by the magnetic moment (Table 1). The pyridine was removed only at 400° under very low pressure, whereupon, provided oxygen was absent, a dark purple sublimate of phthalocyanine chromium(II) (II) was obtained. This compound (II), if regarded as a planar 4-co-ordinate complex of bivalent chromium, would belong to a rare class of compound: however, the magnetic properties (Table 1)—low moment and large negative value of θ—indicate that there is electron-spin coupling between chromium atoms. Therefore, there is some degree of bonding between them and they may be regarded as effectively in a 6-co-ordinate lattice. The thinness of the unit cell, determined as 3·4 Å by electron diffraction, compared with ~4·7 Å in many bivalent metal phthalocyanines,[6] is in agreement with chromium–chromium interaction.

The phthalocyanine chromium(II) (II) tended to be oxidised in air, but the dipyridine complex (V) was stable, as it was also in pyridine solution in the absence of acid. Addition of acid resulted in rapid oxidation and transformation into the 6-co-ordinate hydrated chromium(III) state, the light absorption indicating that the previously encountered dipyridinium salt (VIII; M = C_5H_6N) was formed. If sodium hydroxide (in excess of the acid) was then added to the pyridine solution, no reduction occurred. Nor did reduction occur when the hydroxoaquochromium(III) complex (VII) was treated with acid-free pyridine—again the dipyridinium salt (VIII) resulted. Evidently, the chromium has to be in the 4-co-ordinate state, as in phthalocyanine chromium(III) hydroxide (IV), before it can be approached and reduced by the pyridine. It is also evident that displacement of the pyridine by water is strongly catalysed by acid, and the metal then returns to the normally more stable tervalent state. On addition of sodium dithionite to the dipyridinium

[5] Caglioti, Sartori, and Scrocco, *J. Inorg. Nuclear Chem.*, 1958, **8**, 87.
[6] Linstead and Robertson, *J.*, 1936, 1736.

salt (VIII) in pyridine, the green solution became blue and then purple, the measured light absorption changes indicating that reduction occurred to the chromium(II) state and then to a hydrophthalocyanine complex. Aerial oxidation reversed these changes, as expected.

Magnetic Moments.—These were measured for the pure compounds by the Gouy method over the temperature range 110—295° K. Each compound obeyed the Curie–Weiss law. In Table 1, the effective moment [7] at room temperature is given together with the theoretical value required by each structure, inner orbital bonding being assumed. The experimental moments support the assigned structures unambiguously except for phthalocyanine chromium(II) (II) and the disodium salt (VIII; M = Na). In these two cases the plots give a large intercept θ on the temperature axis. The probable significance for the chromium(II) complex has already been discussed; that for the disodium salt is at present unclear.

Light Absorptions.—For reasons of symmetry, the infrared spectra of phthalocyanine complexes of closely related transitional metals should be similar. The spectra of the established square-planar cobalt(II) and iron(II) complexes [1,6] are indeed very much alike, there being 15 corresponding maxima in the 3—14 μ region (Table 2). Within small limits, 13 of these maxima are common also to the spectrum of phthalocyanine chromium(III) hydroxide, which is excellent support for its constitution (IV), and 12 of these maxima are common to the spectra of all of the other phthalocyanine chromium complexes. There are additional vibrational modes in the latter because of the ligand groupings in the fifth and sixth co-ordination positions and there is a rough correlation between spectral and chemical complexity, but only the few assignments already mentioned can readily be made. In the spectra of the hydrated and hydroxylated complexes there are bands in the 1400—950 cm.$^{-1}$ region which may represent O–H deformations, whilst in the spectra of the pyridine-containing complexes there are bands in the 1600—1480 cm.$^{-1}$ region and near 1215 cm.$^{-1}$ which are probably pyridine skeletal vibrations. The diacetic complex appears best represented by the constitution (IX; R = OAc, R′ = HOAc) because of the similarity of its infrared spectrum to those of the preceding 6-co-ordinate complexes listed in Table 2. The dichloro-complex, on the other hand, has a more complex spectrum suggestive of a major structural difference, and therefore the constitution (X) is preferred, in which the phthalocyanine ring system is protonated.

TABLE 3. *Light absorptions* (230—1000 mμ) (*in methanol unless otherwise indicated*).

Compound	$\lambda_{max.}$ (mμ), with $\log_{10}\varepsilon$ in parentheses								
$PcCr^{III}\cdot OH$ [a]	689	621	502			347			
	(4·92)	(4·14)	(3·91)			(4·62)			
$PcCr^{III}(H_2O)_2\cdot OH$	676	610	502	477		344			268
	(5·17)	(4·48)	(4·05)	(3·99)		(4·60)			(4·48)
$PcCr^{III}(MeOH)_2\cdot OH$	670	605	505	475		340			
	(5·11)	(4·40)	(3·82)	(3·79)		(4·55)			
$2Na^+[PcCr^{III}(O)OH]^{2-}$ [b]	669	604		475		337		278	268
	(5·25)	(4·47)		(3·56)		(4·71)		(4·59)	(4·63)
$K^+[PcCr^{III}(OH)CN]^-$ [c]	677	611	515			345	321	308	271
$K^+[PcCr^{III}(CN)_2]^-$ [d]	675	615	518	490	380	345	322	309	258
$K^+[PcCr^{III}(SCN)_2]^-$ [d]	682	617	511			349		298	270
$HPcCr^{III}Cl_2$ [e]	682	615	507	495	355	347		282	
	(5·15)	(4·30)	(4·03)	(3·93)	(4·70)	(4·71)		(4·57)	
$PcCr^{II},2py$ [f]	687	632	560	525	500	345			
	(4·85)	(4·20)	(3·70)	(3·86)	(3·70)	(4·59)			

[a] In PhCl; and in propylene carbonate which is transparent to 230 mμ. [b] +0·25% NaOH. [c] Intensities not measured because of hydrolysis. [d] See text. [e] +trace of HCl. [f] In pyridine.

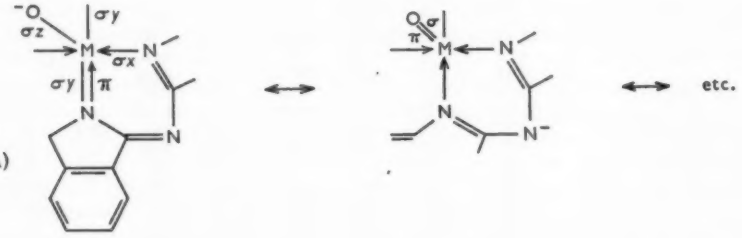
The visible and near-ultraviolet absorption characteristics of the phthalocyanine chromium complexes are listed in Table 3. The use of methanol as a solvent is noteworthy and reflects the greater solubility of the 6-co-ordinate complexes over the majority of

[7] Figgis and Nyholm, *J.*, 1959, 331.

4-co-ordinate phthalocyanine transition-metal derivatives. The present spectra are typical in that the most intense band is in the visible region at 670—690 mμ with the second most intense band at 330—350 mμ.[8] All of the 6-co-ordinate chromium complexes have subsidiary maxima which are atypical. These new bands (in the blue and/or ultraviolet) must result (ultimately) from electronic interactions of the groupings in the fifth and sixth co-ordination positions with the rest of the system. This may be likened to cross-conjugation superimposed on the phthalocyanine chromium chromophore so that new partial chromophore bands are to be expected.

Comparison of present results (Table 3) with data given by Williams *et al.*[9] for octahedral protoporphyrin iron(II) complexes suggests that the weakish absorption band of our chromium complexes in the 502—518 mμ region may result from a π–π^* transition. Williams *et al.* point out that the energy of such a transition will be affected by the degree of coupling between d_ϵ electrons on the metal with π-states of the macrocycle. Good π-acceptor ligands in the fifth and sixth co-ordination positions will reduce or prevent the coupling, so reducing the electron density in the π-states of the porphyrin. The absorption is then expected to move to longer wavelengths (and *vice versa* for π-donor ligands). This is indeed as observed for the symmetrical phthalocyanine chromium complexes, the ligand sequence H_2O, MeOH, Cl^-, CNS^-, CN^- resulting in the bathochromically changing sequence 502, 505, 507, 511, 518 mμ (see Table 3).

Perpendicular Conjugation.—This idea[3] arose from attempts to explain the properties of the octahedral phthalocyanine chromium and manganese complexes. That the complexes $PcCr^{III}(H_2O)\cdot OH$ (VII) and $PcMn^{IV}(OH)_2$[10] each behaved as a *di*basic acid was unexpected. It seemed that there must be means for stabilizing the anions $[PcCr(O)OH]^{2-}$ and $[PcMnO_2]^{3-}$ and that this could be achieved through distribution of the negative charge (formally on oxygen) over the π-electron system of the macrocycle. Such a sharing of charge with the aromatic ring is accepted, for example, in the phenoxide anion. For the sharing to be possible in the phthalocyanine complex anions, it was necessary to assume that there was conjugation between the mutually perpendicular phthalocyanine and oxy-groups. How this might be possible, through simple overlap of a d_{xz}(or d_{yz})-orbital of the metal with *p*-orbitals of nitrogen and oxygen along the *x*(or *y*)- and *z*-axes has been indicated.[3,11] It was pointed out that the sets of canonical structures which might then be written could not be hybridised because of the symmetry of the *d*-orbitals. Nevertheless the limited conjugation allows the required distribution of negative charge, as indicated by the partial formulæ (A).



The process indicated in (A) could operate only if a d_{xz}(or d_{yz})-orbital of the metal were vacant. If the anion is an inner orbital complex (as is most probable), then the perpendicular conjugation must be through 4*d*-orbitals (which are capable of accepting electrons

[8] Linstead, *J.*, 1953, 2873.
[9] Cowan, Drake, and Williams, *Discuss. Faraday Soc.*, 1959, **27**, 217.
[10] To be described later in full.
[11] Elvidge and Lever, *Proc. Chem. Soc.*, 1959, 171.

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for π-bonding). (It is much less likely that the anion is spin-free and that a $3d_{xz}$- or $3d_{y}$-orbital is freed by promotion of an electron to one of the vacant $3d_{y}$-orbitals, as previously implied.[3]) 4*d*-Orbitals are diffuse and so the overlap with *p*-orbitals of the ligand atoms would become increasingly poor along the first-row transition-metal series from titanium to copper, and perpendicular conjugation in suitable derivatives might vanish by about cobalt. It is perhaps significant that the light absorptions (visible and ultraviolet) of the analogues of vitamin B_{12} (B_{12a}, etc.) are closely similar,[12] but that those of the octahedral phthalocyanine chromium (and manganese) complexes show variations which appear too large (Table 3) to be ascribed solely to inductive effects of the ligands. There may be evidence here of the operation of perpendicular conjugation.

Williams's observations [9,13] concerning the spectra of some octahedral porphyrin complexes appear to provide evidence for perpendicular conjugation in these compounds. Chatt and his co-workers [14] explain the physical properties of some 4-co-ordinate platinum complexes in terms of a " *cis*-effect," whereby the electron push or pull of a ligand affects the bond strength of the ligand *cis* to it, *i.e.*, attached to the metal in the perpendicular direction. Thus electronic effects can certainly be transmitted through $3d_{\epsilon}$-orbitals, but this only becomes conjugation if one or other of the ligands is unsaturated so that the effects can be carried further. Such a case would differ from the example of perpendicular conjugation presented by the phthalocyanine complexes because all of the atoms concerned would be coplanar. The essential point concerning the octahedral phthalocyanine derivatives is that conjugation is postulated through a series of atoms which are not all coplanar (see A).

Craig's treatment [15] of conjugation in the phosphonitrilic halides, from which our postulate of perpendicular conjugation is ultimately derived,[3] proposed π-bond formation by the overlap of each nitrogen *p*-orbital with the adjacent phosphorus d_{xz}-orbital. Interactions with the phosphorus d_{yz}-orbital were taken to be negligible. Recently, Dewar *et al.*[16] concluded that this was unjustified and that the pair of phosphorus d_{xz}- and d_{yz}-orbitals should be combined linearly to give two new d_{π}-orbitals, each of which would overlap with just one of the adjacent nitrogen *p*-orbitals. This treatment thus leads to the conclusion that each nitrogen atom is at the mid-point of a 3-centre π-bond formed with the two neighbouring phosphorus atoms, and that the conjugation is broken at each phosphorus atom so that there is no through conjugation. It was further suggested that no significant through conjugation should therefore be observed in other examples of d_{π}–p_{π} π-bonding. That electronic effects appear to be transmitted perpendicularly through the *d*-orbitals of suitable metals must nevertheless be admitted, and their magnitude suggests through conjugation—which is indeed implied by the interpretation of the spectra of octahedral protoporphyrin iron(II) complexes given by Williams and his colleagues.[9] A compromise explanation seems necessary. Further experimental evidence is needed and is being sought.

Experimental

As in previous work in this series, the progress of reactions and of purifications was followed by quantitative measurements of visible-light absorption.

Phthalocyanine Chromium(III) *Hydroxide* (IV).—An intimate mixture of chromic acetate (3 g.) and phthalonitrile (6 g., purified) was heated to 270°. After 15 min., the melt thickened and was allowed to cool. The solid was powdered and triturated in turn with benzene, methanol, water, methanol, and ether. The product (8 g.), mainly phthalocyanine chromium(II) and phthalocyanine chromium(III) acetate, was heated at 400°/10^{-6} mm., whereupon the

[12] Kaczka, Wolf, Kuehl, and Folkers, *J. Amer. Chem. Soc.*, 1951, **73**, 3569.
[13] Williams, *Chem. Rev.*, 1956, **56**, 299.
[14] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.
[15] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *J.*, 1959, 997.
[16] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

chromous complex sublimed but underwent oxidation. Further sublimation afforded *phthalocyanine chromium*(III) *hydroxide* as long purple needles (Found: C, 66·1, 66·0; H, 3·55, 3·0; Cr, 9·4, 9·0; N, 19·4. $C_{32}H_{17}CrN_8O$ requires C, 66·1; H, 2·95; Cr, 8·95; N, 19·3%). On quantitative oxidation [17] the pigment consumed 1·03 atom-equiv. of O ($PcCr^{III}OH$ requires 1·0 atom-equiv. of O).[18]

Phthalocyanine Chromium(III) *Acetate* (I).—The preceding hydroxide (50 mg.) was kept with acetic anhydride for 24 hr. The product was washed with anhydrous ether and dried at 180°/15 mm. to give the *acetate* (Found: C, 65·4; H, 3·1; Cr, 8·55. $C_{34}H_{19}CrN_8O_3$ requires C, 65·5; H, 3·1; Cr, 8·3%).

Phthalocyanine Dimethanolchromium(III) *Hydroxide* (III; R = R′ = MeOH).—Phthalocyanine chromium(III) hydroxide (50 mg.) was heated with methanol (7 c.c.) under reflux for 2 hr. The *complex* was washed with anhydrous ether and dried in a desiccator (yield, 54 mg.) (Found: C, 63·5; H, 3·9; Cr, 8·3; N, 16·9. $C_{34}H_{25}CrN_8O_3$ requires C, 63·25; H, 3·9; Cr, 8·1; N, 17·4%). When heated at 180°/20 mm. for several hr., this complex afforded phthalocyanine chromium(III) hydroxide, as indicated by the infrared absorption.

Phthalocyanine Aquomethanolchromium(III) *Hydroxide* (III; R = H_2O, R′ = MeOH).—Phthalocyanine chromium(III) hydroxide (100 mg.) was kept with acetic acid (4·5 c.c.), water (3 c.c.), and methanol (1 c.c.) at 90° for 5 hr. After being washed with water, methanol, and then ether, the *complex* was dried in a desiccator (yield, 105 mg.) (Found: C, 63·1; H, 3·55; Cr, 8·0. $C_{33}H_{23}CrN_8O_3$ requires C, 62·75; H, 3·9; Cr, 8·25%). At 180°/20 mm., this complex lost weight (4%) and afforded phthalocyanine hydroxoaquochromium(III) with infrared absorption identical with that of authentic material (see below).

Phthalocyanine Diaquochromium(III) *Hydroxide* (III; R = R′ = H_2O) *and the 6-Co-ordinate Complex* (VII).—Phthalocyanine chromium(III) hydroxide (50 mg.) was warmed with 3 : 1 : 4 aqueous-ethanolic acetic acid at 95° for 3 hr. Alternatively the hydroxoaquochromium(III) compound (VII) (80 mg.) was suspended in water (5 c.c.) at 95° for 4 hr. The *complex* was washed with water, methanol and ether, and dried in a desiccator (yield, 97%) (Found: C, 62·2; H, 3·7; Cr, 8·6. $C_{32}H_{21}CrN_8O_3$ requires C, 62·2; H, 3·4; Cr, 8·4%). Sublimation of the complex (36 mg.) at 400°/10^{-6} mm. afforded phthalocyanine chromium(III) hydroxide (20 mg.) identified by its infrared spectrum. At 180°/20 mm., however, the complex yielded *phthalocyanine hydroxoaquochromium*(III) (VII) (Found: C, 64·4, 64·2; H, 3·7, 3·5; Cr, 8·6; N, 18·3. $C_{32}H_{19}CrN_8O_2$ requires C, 64·1; H, 3·2; Cr, 8·7; N, 18·7%). Sublimation of this at 400°/10^{-6} mm. afforded phthalocyanine chromium(III) hydroxide (correct infrared spectrum) in 60% yield (Found: C, 66·0; H, 3·0%).

Phthalocyanine Acetatoaquochromium(III) (IX; R = OAc, R′ = H_2O).—Powdered phthalocyanine hydroxoaquochromium(III) (50 mg.) was kept with acetic anhydride (1 c.c.) for 24 hr. The green powder (100%) was washed with ether and dried at 180°/20 mm., so affording the *complex* (Found: C, 63·4; H, 3·5; Cr, 8·5. $C_{34}H_{21}CrN_8O_3$ requires C, 63·6; H, 3·3; Cr, 8·1%). An identical product (infrared spectrum) resulted from treatment of phthalocyanine chromium(III) hydroxide with 70% aqueous acetic acid at 90° for 2 hr.

Phthalocyanine propionatoaquochromium(III) (IX; R = O·CO·Et, R′ = H_2O), formed by keeping phthalocyanine hydroxoaquochromium(III) with propionic anhydride for 1 week, was washed with ether and dried at 180°/15 mm. (Found: C, 63·85; H, 3·9; Cr, 7·6. $C_{35}H_{23}CrN_8O_3$ requires C, 64·1; H, 3·55; Cr, 7·9%).

Phthalocyanine Acetato(acetic acid)chromium(III) (IX; R = OAc, R′ = HOAc).—Phthalocyanine hydroxoaquochromium(III) (VII) (50 mg.), or phthalocyanine chromium(III) hydroxide (IV), was refluxed in acetic anhydride (10 c.c.) for 1·5 hr. The *complex* (96%) was washed with methanol and ether, and dried at 180°/15 mm. (Found: C, 63·5; H, 3·7; Cr, 7·7. $C_{36}H_{23}CrN_8O_4$ requires C, 63·25; H, 3·4; Cr, 7·6%).

Phthalocyanine Acetatomethanolchromium(III) (IX; R = OAc, R′ = MeOH).—Phthalocyanine chromium(III) hydroxide (30 mg.), methanol (5 c.c.), and acetic acid (3 c.c.) were refluxed together for 3 hr. The green *complex* (30 mg.) was washed with methanol and ether, and dried in a desiccator (Found: C, 63·8; H, 3·9; Cr, 7·8. $C_{35}H_{23}CrN_8O_3$ requires C, 64·1; H, 3·55; Cr, 7·9%). At 180°/20 mm., this complex was converted into phthalocyanine chromium(III) acetate (Found: C, 65·2; H, 3·1; Cr, 8·5%).

Hydrogen [*Phthalocyanine Dichlorochromate*(III)] (X).—Dry hydrogen chloride was passed

[17] Elvidge, *J.*, 1961, 869.
[18] Cf. Dent, Linstead, and Lowe, *J.*, 1934, 1036.

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into a refluxing suspension of phthalocyanine chromium(III) hydroxide (180 mg.) in methanol (15 c.c.) for 3 hr. The very dark green *product* (180 mg.) was dried at 180°/20 mm. (Found: C, 60·5; H, 3·3; Cl, 10·7; Cr, 8·3; N, 17·0. $C_{32}H_{17}Cl_2CrN_8$ requires C, 60·4; H, 2·7; Cl, 11·1; Cr, 8·2; N, 17·6%).

Potassium [*Phthalocyanine Hydroxocyanochromate*(III)] (VI).—Phthalocyanine chromium(III) hydroxide (80 mg.), methanol (5 c.c.), butanol (5 c.c.), and potassium cyanide (80 mg.) were refluxed together for 8 hr., and the mixture was then filtered. During 1 week at 2°, the filtrate deposited elongated prisms of the *complex* (35 mg.) which was washed with cold water, methanol and ether, and dried at 180°/20 mm. (Found: C, 61·5; H, 3·05; Cr, 7·7; K, 5·9; N, 19·4. $C_{33}H_{17}CrKN_9O$ requires C, 61·3; H, 2·65; Cr, 8·0; K, 6·05; N, 19·5%).

Disodium [*Phthalocyanine Oxohydroxochromate*(III)] (VIII; M = Na).—Powdered phthalocyanine hydroxoaquochromium(III) (VII) (100 mg.) was shaken with 1% sodium hydroxide in ethanol (5 c.c.) for 24 hr. The purple crystals of the complex *salt* were washed rapidly with ethanol and then with ether, and dried at 180°/20 mm. (yield, 90 mg.) (Found: C, 60·1, 59·7; H, 3·2, 3·2; Cr, 7·7; Na, 7·2. $C_{32}H_{17}CrN_8Na_2O_2$ requires C, 59·7; H, 2·7; Cr, 8·1; Na, 7·15%).

Diammonium [*Phthalocyanine Oxohydroxochromate*(III)] (VIII; M = NH_4).—Liquid ammonia (~10 c.c.) was filtered on to the hydroxoaquo-complex (VII) (50 mg.), cooled with liquid ammonia. After 5 hr., the ammonia had evaporated and the *salt* was then dried in a desiccator (Found: C, 61·3; H, 4·0; Cr, 7·3. $C_{32}H_{25}CrN_{10}O_2$ requires C, 60·8; H, 3·95; Cr, 8·2%). At room temperature, the salt slowly evolved ammonia.

Dipyridinium [*Phthalocyanine Oxohydroxochromate*(III)] (VIII; M = pyH).—The powdered hydroxoaquo-complex (VII) (100 mg.) was kept with pyridine (1 c.c.) for 24 hr. and the resulting jade-green crystals (125 mg.) of the *salt* were washed with ether and dried at 150°/20 mm. (Found: C, 66·6; H, 3·95; Cr, 7·0. $C_{42}H_{29}CrN_{10}O_2$ requires C, 66·6; H, 3·9; Cr, 6·9%). Alternatively, phthalocyanine chromium(III) hydroxide (80 mg.) was shaken for 24 hr. with pyridine (4 c.c.), acetic acid (3 c.c.), and water (0·5 c.c.). The product (100 mg.), after being washed with ether and dried at 150°/15 mm., had an infrared spectrum indistinguishable from that given by the preceding salt.

Phthalocyanine Dipyridinechromium(II) (V).—Dried, powdered phthalocyanine chromium(III) hydroxide (IV) (135 mg.) was shaken under nitrogen with pyridine (2 c.c., freshly distilled from barium oxide). After 24 hr., the olive-green chromium(II) *complex* was washed with anhydrous ether and dried at 150°/15 mm. (yield, 146 mg.) (Found: C, 69·45; H, 4·0; Cr, 7·2; N, 19·2. $C_{42}H_{26}CrN_{10}$ requires C, 69·8; H, 3·6; Cr, 7·2; N, 19·4%).

Phthalocyanine Chromium(II) (II).—Sublimation of the preceding complex at 400° in nitrogen at 10^{-6} mm. afforded the chromium(II) *complex* as dark purple needles (Found: C, 67·7, 68·45; H, 3·0, 3·1; Cr, 9·3, 9·2. $C_{32}H_{16}CrN_8$ requires C, 68·1; H, 2·9; Cr, 9·2%). On quantitative oxidation,[17] the complex consumed 1·56, 1·33 atom-equiv. of O ($PcCr^{II}$ requires 1·50 atom-equiv. of O).

We thank the Department of Scientific and Industrial Research for a maintenance grant (to A. B. P. L.) and Imperial Chemical Industries Limited for generous gifts of phthalonitrile. Dr. I. S. Kerr of this College very kindly made the electron-diffraction measurements on chromous phthalocyanine.

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[*Received, July 27th*, 1960.]

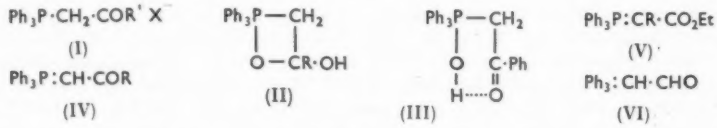
246. *The Phosphobetaines: Preparation and Properties.*

By S. Trippett and D. M. Walker.

β-Ketoalkyltriphenylphosphonium salts have been prepared by the action of esters, including formates, and of acid chlorides on Wittig reagents. The phosphobetaines $Ph_3P{:}CHR$ (R = CN, $CO{\cdot}NH_2$, CHO) react with aldehydes, but not with ketones, to give the corresponding αβ-unsaturated compounds.

The groups R, in the phosphorane $R_3P{:}CXY$ taking part in the Wittig olefin synthesis, may be phenyl or methyl. In the phosphobetaines $Ph_3P{:}CH{\cdot}COR$, replacement of phenyl by methyl does not give useful reactivity towards ketones.

Michaelis and Köhler [1] showed that when the phosphonium salts $Ph_3P{\cdot}CH_2{\cdot}COR^+ X^-$ (R = Me or Ph), prepared by the action of triphenylphosphine on the corresponding α-halogeno-ketones, were treated with aqueous alkali, stable halogen-free compounds were obtained. They were termed phosphobetaines and assigned the structure (II). Wittig and Schöllkopf [2] obtained the phosphonium salt (I; R = Ph) by reaction of methylenetriphenylphosphorane with ethyl benzoate, and, on the basis of infrared evidence (lack of hydroxyl absorption at 3 μ and of carbonyl absorption below 6·5 μ) gave to the betaine the hydrogen-bonded structure (III). Ramirez and Dershowitz,[3] however, showed the true molecular formulæ of these betaines to be less by a molecule of water than those required by structures (II) and (III), and formulated them as true phosphoranes (IV; R = Me or Ph), stabilised by resonance. In agreement with this, the betaines with benzaldehyde gave triphenylphosphine oxide and benzylidene-acetone or -acetophenone.



They did not react with ketones. The betaines (V; R = H or Alk), prepared by the action of alkali on the phosphonium salts, have also been used [4] in Wittig reactions with aldehydes, particularly in the carotenoid field. We have previously described [5] the preparation of $Ph_3P{:}CH{\cdot}CO{\cdot}NH_2$ and of $Ph_3P{:}CH{\cdot}CN$; these have now been shown to react with aldehydes to give αβ-unsaturated amides and nitriles, but neither these, nor the ethoxycarbonyl betaine (V; R = H), reacted with ketones.*

We have now prepared the aldehyde betaine (VI) by addition of methylenetriphenylphosphorane to an excess of ethyl formate, having failed in attempts to quaternise triphenylphosphine with chloroacetaldehyde or with bromoacetal. After our preliminary communication,[6] Dr. Martin Grayson of the American Cyanamid Co. kindly informed us that success in the quaternisation with chloroacetaldehyde depends upon having anhydrous conditions, and that a solution of the chloroacetaldehyde–water azeotrope in chloroform can be made anhydrous by distillation of the chloroform–water azeotrope. This method makes the phosphorane (VI) readily available by the action of aqueous alkali or ethanolic

* *Added in Proof.*—See, however, Sugasawa and Matsno *Chem. and Pharm. Bull.* (*Japan*), 1960, **8**, 819, for the reaction between ethoxycarbonylmethyltriphenylphosphonium bromide and cyclohexanones in methanol at room temperature in the presence of sodium methoxide

[1] Michaelis and Köhler, *Ber.*, 1899, **32**, 1566.
[2] Wittig and Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.
[3] Ramirez and Dershowitz, *J. Org. Chem.*, 1957, **22**, 41.
[4] Isler, Gutmann, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1957, **40**, 1242.
[5] Trippett and Walker, *J.*, 1959, 3874.
[6] Trippett and Walker, *Chem. and Ind.*, 1960, 202.

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triethylamine on the phosphonium chloride. Our original difficulties may have been due to the lack of reactivity of chloroacetaldehyde hydrate, $Cl{\cdot}CH_2{\cdot}CH(OH)_2$, or to the fact that the phosphonium chloride $Ph_3P{\cdot}CH_2{\cdot}CHO^+Cl^-$ decomposes to triphenylphosphine oxide when heated in the presence of water.

Formylmethylenetriphenylphosphorane is stable to hydroxylic solvents at room temperature. When refluxed in benzene with an aldehyde, it gave triphenylphosphine oxide and the corresponding αβ-unsaturated aldehyde:

$$R{\cdot}CHO + Ph_3P{:}CH{\cdot}CHO \longrightarrow R{\cdot}CH{:}CH{\cdot}CHO + Ph_3PO$$

Thus benzaldehyde gave cinnamaldehyde (60%), n-heptaldehyde gave non-2-enal (81%), and the dialdehyde (VII) gave the dialdehyde (VIII). However, the phosphorane (VI) did not react with ketones.

(VII) (VIII)

1-Formylethylidenetriphenylphosphorane was similarly prepared by the action of ethyl formate on ethylidenetriphenylphosphorane. With aldehydes, it gave the unsaturated aldehydes $R{\cdot}CH{:}CMe{\cdot}CHO$.

Reaction of Wittig reagents with esters other than formates is in general slow and gives poor yields of β-keto-alkylphosphonium salts. With acid chlorides, a more rapid reaction gives the β-keto-alkylphosphonium chlorides in 30—50% yield. Benzylidenetriphenylphosphorane with esters gave only unchanged starting materials; with acid chlorides, the phosphonium chlorides $Ph_3P{\cdot}CHPh{\cdot}COR^+Cl^-$ were obtained.

The β-keto-alkylphosphonium salts were unchanged on treatment with sodium borohydride or diborane, and on attempted Meerwein–Ponndorf reduction or hydrogenation with a platinum catalyst. With zinc and acetic acid, they, and the phosphobetaines, gave triphenylphosphine and a ketone (~95%). The reaction of Wittig reagents with acid chlorides, followed by reduction with zinc and acetic acid, constitutes a formal ketone synthesis.

$$Ph_3P{\cdot}CH_2{\cdot}COR^+\,X^- \xrightarrow[AcOH]{Zn} Ph_3P + CH_3{\cdot}COR$$

Of the stable phosphoranes $Ph_3P{:}CH{\cdot}COR$ so far prepared, none reacts with ketones. This is a failure in the first step of the Wittig reaction, nucleophilic attack on carbon, not in the subsequent elimination of phosphine oxide. It seemed possible that successive replacement of the phenyl groups by methyl might increase the nucleophilic character of the phosphoranes to the point where this reaction became possible. Wittig and Reiber [7] reported that methylenetrimethylphosphorane, $Me_3P{:}CH_2$, gave with benzophenone the betaine $Ph_2C(\cdot O^-){\cdot}CH_2{\cdot}PMe_3^+$, but that this would not eliminate trimethylphosphine oxide, and it was suggested [2] that this was because hyperconjugation of methyl reduced the oxygen-affinity of the phosphorus atom. Johnson and LaCount,[8] however, showed later that fluorenylidenetrimethylphosphorane with *p*-nitrobenzaldehyde gave 4-nitrobenzylidenefluorene, and, more recently, the same workers [9] have described similar successful Wittig reactions using fluorenylidenetributylphosphorane. These are very favourable cases for olefin formation, and it seemed desirable to investigate the general Wittig reaction with mixed methyl-phenyl-phosphoranes.

It soon became apparent that the Wittig olefin synthesis is not dependent on the nature of the groups R in the participating phosphorane $R_3P{:}CXY$. The series of phosphoranes $Me_{3-n}Ph_nP{:}CHPh$ ($n = 0$—3) all gave benzylidenefluorene on reaction with fluorenone, and the phosphoranes with $n = 0$ or 1 reacted with cyclohexanone to give

[7] Wittig and Reiber, *Annalen*, 1949, **562**, 177.
[8] Johnson and LaCount, *Chem. and Ind.*, 1959, 52.
[9] Johnson and LaCount, *Tetrahedron*, 1960, **9**, 130.

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benzylidenecyclohexane. Repetition of the unsuccessful reaction reported by Wittig and Reiber between methylenetrimethylphosphorane and benzophenone gave 1,1-diphenylethylene (40%). However, the elimination of trimethylphosphine oxide, required to afford an unconjugated double bond, is relatively difficult. Methylenetrimethylphosphorane and cyclohexanone in boiling tetrahydrofuran gave no detectable methylenecyclohexane: in 2,2′-dimethoxydiethyl ether at 100°, 15% of the desired olefin was formed.

Among the stable phosphoranes $Me_{3-n}Ph_nP{:}CH{\cdot}COR$, the gradual replacement of the phenyl by methyl reduced the stability to water, and the only complete series isolated was that derived from phenacyl bromide, *i.e.*, where R = Ph and $n = 0$—**3**. Even here, the early members ($n = 0$, 1) were prepared at 0°, and were hydrolysed rapidly at room temperature in contact with water. High yields of benzylideneacetophenone were obtained on reaction with benzaldehyde, but none of the series reacted with ketones. These phosphoranes (with R = Me, OEt, or H; and $n = 0$—2) could not, in general, be prepared by the action of alkali at 0° on solutions of the quaternary salts in chloroform, the phosphine oxide being formed in each case. Attention was therefore turned to the generation of the phosphoranes *in situ*, by the action of a suitable base on the phosphonium salts in solution with the carbonyl compound.

(Ethoxycarbonylmethyl)dimethylphenylphosphonium bromide, with pyridine and benzaldehyde in boiling nitromethane, gave, after hydrolysis, cinnamic acid (22%), but the same conditions were not successful with the corresponding trimethylphosphonium salt. Sodium ethoxide and piperidine were also ineffective in promoting the latter condensation, but, in the presence of triethylamine, (ethoxycarbonylmethyl)trimethylphosphonium bromide and benzaldehyde gave, after hydrolysis, a 48% yield of cinnamic acid. Under the same conditions, (ethoxycarbonylmethyl)trimethylphosphonium bromide did react with cyclohexanone, but the yield of cyclohexylideneacetic acid was only 3%. We therefore concluded that the increased nucleophilic character of the phosphobetaines on replacement of the phenyl by methyl had not given a useful reactivity towards ketones.

Experimental

Unless otherwise stated, light petroleum refers to the fraction of b. p. 60—80°. All experiments were carried out under oxygen-free nitrogen.

Reaction of Benzaldehyde with Cyanomethylenetriphenylphosphorane.—A solution of benzaldehyde (1·65 g.) and the phosphorane (4·7 g.) in benzene (50 ml.) was refluxed for 12 hr., light petroleum (150 ml.) added, and the solution set aside at room temperature to crystallise. Filtration then gave triphenylphosphine oxide (4·2 g.). Evaporation of the mother-liquors and distillation of the residue gave cinnamonitrile (1·3 g.), b. p. 137—138°/19 mm., $\lambda_{max.}$ 4·45,10·34 μ.

Reaction of Benzaldehyde with Carbamoylmethylenetriphenylphosphorane.—A solution of benzaldehyde (0·33 g.) and the phosphorane (1 g.) in benzene (25 ml.) was refluxed for 20 hr. and the solvent evaporated. Extraction of the residue with hot light petroleum gave, on cooling, triphenylphosphine oxide, m. p. 155°. Evaporation of the mother-liquors and sublimation of the residue gave cinnamamide (0·1 g.), m. p. 146—147° (Found: N, 9·2. Calc. for C_9H_9NO: N, 9·5%).

n-Heptaldehyde under the same conditions gave the amide of non-2-enoic acid (14%), m. p. (from light petroleum) 130—131° (Found: C, 69·9; H, 10·9; N, 9·4. Calc. for $C_9H_{17}NO$: C, 69·7; H, 10·9; N, 9·0%).

Formylmethyltriphenylphosphorane.—(*a*) To a stirred suspension of methyltriphenylphosphonium bromide (10·7 g.) in ether (100 ml.), ethereal 1·16N-butyl-lithium (25 ml.) was added, and the solution was stirred for 0·5 hr. and slowly added to a stirred solution of ethyl formate (2·7 g.) in ether (50 ml.). After 0·5 hr., the solution was extracted with dilute hydrochloric acid (2 × 100 ml.), and the combined extracts were made alkaline with dilute sodium hydroxide and extracted with benzene (3 × 200 ml.). Evaporation of the extracts gave *formylmethylenetriphenylphosphorane* (6·1 g.), m. p. (from acetone) 186—187° (decomp.) (Found: C, 78·9; H, 5·8. $C_{20}H_{17}OP$ requires C, 78·9; H, 5·6%).

(*b*) *Chloroacetaldehyde–water azeotrope (b. p. 85·5°; 96·5 g.) was added to chloroform

* Personal communication from Dr. M. Grayson.

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(1·5 l.), and the chloroform–water azeotrope (b. p. 56°; 800 ml.) was removed through a column until the solution was anhydrous. Triphenylphosphine (131 g.) was added to the resulting clear solution, which, after refluxing for 5 hr., was set aside at room temperature overnight. Removal of solvent under reduced pressure then gave crude *formylmethyltriphenylphosphonium chloride* (166·5 g.), m. p. (from chloroform–ethyl acetate) 212—213° (decomp.) (Found: C, 70·2; H, 5·7; P, 8·85. $C_{20}H_{18}ClOP$ requires C, 70·5; H, 5·3; P, 9·1%). Treatment of the phosphonium salt in ethanol with triethylamine, or in water with dilute sodium hydroxide, gave the above phosphorane, m. p. 187—188° (decomp.).

Reaction of Formylmethylenetriphenylphosphorane with Aldehydes.—(a) *Benzaldehyde.* A solution of benzaldehyde (0·86 g.) and the phosphorane (2·6 g.) in benzene (50 ml.) was refluxed for 24 hr., solvent removed under reduced pressure, and the residue extracted with a little cold ether. The residue crystallised from light petroleum to give triphenylphosphine oxide (1·6 g.), m. p. 154—155°. Evaporation of the extract gave an oil (1·06 g.; $\lambda_{max.}$ 286 mμ) which gave a 2,4-dinitrophenylhydrazone (2·1 g.), m. p. and mixed m. p. with cinnamaldehyde 2,4-dinitrophenylhydrazone, 253°.

Under the same conditions, n-heptaldehyde gave an oil ($\lambda_{max.}$ 224 mμ) which gave *non-2-en-1-al 2,4-dinitrophenylhydrazone*, m. p. (from methanol) 117—118° (Found: C, 56·2; H, 6·25; N, 17·1. $C_{15}H_{20}N_4O_4$ requires C, 56·2; H, 6·25; N, 17·5%).

(b) *2,7-Dimethylocta-2,6-dien-4-yne-1,8-dial.* A solution of the dialdehyde (0·55 g.) and formylmethylenetriphenylphosphorane (2·06 g.) in benzene (100 ml.) was refluxed for 16 hr. and solvent then removed under reduced pressure. Counter-current distribution (50 transfers) of the residue in the system benzene–light petroleum–methanol–water (1 : 1 : 1 : 0·5) gave from the leading tubes 4,9-dimethyldodeca-2,4,8,10-tetraen-6-yne-1,12-dial [10] (0·1 g.), m. p. (from acetone–water) 163—164°, $\lambda_{max.}$ 371, 390 mμ (ε 69,450, 67,890 in ethanol).

α-Formylethylidenetriphenylphosphorane.—To a stirred suspension of ethyltriphenylphosphonium iodide (4·1 g.), in ether (100 ml.), ethereal 1·16N-butyl-lithium (9 ml.) was added, and the resulting solution added slowly to a stirred solution of ethyl formate (1 g.) in ether (50 ml.). The suspension was then extracted with dilute hydrochloric acid, and the extract made alkaline with dilute sodium hydroxide and extracted with benzene. Removal of the benzene under reduced pressure, and crystallisation of the residue from benzene–light petroleum, gave *α-formylethylidenetriphenylphosphorane* (1·2 g.), m. p. 220—222° (Found: C, 79·4; H, 6·3. $C_{21}H_{19}OP$ requires C, 79·25; H, 6·0%).

A solution of the phosphorane in chloroform was shaken with dilute hydrochloric acid. Evaporation of the chloroform, and crystallisation of the residue from ethanol–ether, gave *α-formylethyltriphenylphosphonium chloride*, m. p. 231—233° (Found: C, 70·7; H, 5·35. $C_{21}H_{20}ClOP$ requires C, 71·1; H, 5·65%).

Reaction of α-Formylethylidenetriphenylphosphorane with Benzaldehyde.—A solution of benzaldehyde (0·33 g.) and the phosphorane (1 g.) was refluxed for 24 hr., solvent removed under reduced pressure, and the residue extracted with a little cold light petroleum (b. p. 40—60°). Crystallisation of the residue from benzene–light petroleum gave triphenylphosphine oxide (0·8 g.), m. p. 154—155°. Evaporation of the extract gave an oil ($\lambda_{max.}$ 283 mμ) from which *α-methylcinnamaldehyde 2,4-dinitrophenylhydrazone* (0·6 g.), m. p. (from ethyl acetate) 207—208°, was obtained (Found: C, 59·1; H, 4·35. $C_{16}H_{14}N_4O_4$ requires C, 58·9; H, 4·3%).

Under the same conditions, heptaldehyde gave an oil ($\lambda_{max.}$ 227 mμ) which gave *2-methylnon-2-en-1-al 2,4-dinitrophenylhydrazone* (72%), m. p. (from ethanol) 115—116° (Found: C, 57·65; H, 6·75; N, 17·0. $C_{16}H_{22}N_4O_4$ requires C, 57·5; H, 6·6; N, 16·8%).

Reaction of Methylenetriphenylphosphorane with Ethyl Acetate.—To a stirred suspension of methyltriphenylphosphonium bromide (1·8 g.) in ether (60 ml.), ethereal 1·3N-butyl-lithium (4·5 ml.) was added, and the solution was stirred for 0·5 hr. and then added slowly to a stirred solution of ethyl acetate (0·45 g.) in ether (20 ml.). Solvent was removed and the residue extracted with chloroform. The extract was washed with dilute hydrochloric acid, dried, and evaporated. Crystallisation of the residue from ethanol–ether gave acetonyltriphenylphosphonium chloride (16%), m. p. and mixed m. p. 236—237°.

Reaction of Benzylidenetriphenylphosphorane with Acetyl Chloride.—To a stirred suspension of benzyltriphenylphosphonium bromide (2·17 g.) in ether (75 ml.), ethereal 1·3N-butyl-lithium (4 ml.) was added. After 0·5 hr., the resulting solution was added slowly to a stirred solution

[10] Isler, Gutmann, Lindlar, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1956, **39**, 463.

of acetyl chloride (0·4 g.) in ether (25 ml.), and the solvent then removed. The residue was extracted with chloroform and the extract washed with dilute hydrochloric acid and with water, dried, and evaporated. Crystallisation of the residue from aqueous ethanol gave *α-phenylacetonyltriphenylphosphonium chloride* (47%), m. p. 172—173° (Found: C, 72·2; H, 5·75. $C_{27}H_{24}ClOP,H_2O$ requires C, 72·2; H, 5·8%). Addition of dilute sodium hydroxide to the quaternary salt gave *α-phenylacetonylidenetriphenylphosphorane*, m. p. (from aqueous ethanol) 167—168° (Found: C, 81·6; H, 5·7. $C_{27}H_{23}OP$ requires C, 82·0; H, 5·8%).

When a similar procedure was used, benzylidenetriphenylphosphorane and benzoyl chloride gave α-benzoylbenzylidenetriphenylphosphorane,[5] m. p. 191—192°; methylenetriphenylphosphorane with acetyl chloride gave acetonyltriphenylphosphonium chloride (38%), m. p. 235—236°, and with benzoyl chloride gave phenacyltriphenylphosphonium chloride (27%), m. p. 260—261°.

Reduction of Acetonyltriphenylphosphonium Chloride with Zinc and Acetic Acid.—The phosphonium chloride (1·73 g.) was dissolved in chloroform (25 ml.), zinc dust (12 g.) added, and the solution refluxed for 2 hr. during which acetic acid (50 ml.) was added in small portions. Steam-distillation of the residue into a solution of 2,4-dinitrophenylhydrazine in dilute hydrochloric acid gave acetone 2,4-dinitrophenylhydrazone (97%), m. p. and mixed m. p. 128—129°. Ether-extraction of the residue from steam-distillation gave triphenylphosphine (67%), m. p. 79·5°.

In a similar way, phenacyltriphenylphosphonium bromide gave acetophenone 2,4-dinitrophenylhydrazone (95%), m. p. and mixed m. p. 236°, and triphenylphosphine (56%).

Phosphonium Salts derived from Methyldiphenylphosphine.—Methyldiphenylphosphine (b. p. 120—122°/0·2 mm.) was prepared by the reduction of methyldiphenylphosphine oxide with lithium aluminium hydride according to the general instructions of Horner *et al.*[11] The phosphonium salts were prepared by mixing benzene solutions of equimolecular amounts of phosphine and halide at 0°.

Benzylmethyldiphenylphosphonium bromide had m. p. (from chloroform–benzene) 245—246° (Found: C, 64·5; H, 5·35. $C_{20}H_{20}BrP$ requires C, 64·5; H, 5·4%).

Methylphenacyldiphenylphosphonium bromide had m. p. (from benzene–light petroleum) 70—72°, but was very hygroscopic and could not be satisfactorily analysed. A chloroform solution at 0°, shaken with dilute sodium hydroxide, dried, and evaporated, gave *(benzoylmethylene)methyldiphenylphosphorane*, m. p. (from acetone–light petroleum) 123—124° (Found: C, 76·75; H, 6·0. $C_{21}H_{19}OP,\frac{1}{2}H_2O$ requires C, 76·9; H, 6·1%).

Acetonylmethyldiphenylphosphonium chloride had m. p. (from chloroform–ethyl acetate) 170—171° (Found: C, 65·35; H, 6·35. $C_{16}H_{18}ClOP$ requires C, 65·7; H, 6·15%). A chloroform solution at 0°, shaken with dilute sodium hydroxide, dried, and evaporated, gave *acetonylidenemethyldiphenylphosphorane*, m. p. (from benzene–light petroleum) 113—115° (Found: C, 74·55; H, 6·65. $C_{16}H_{17}OP$ requires C, 75·0; H, 6·65%).

(Ethoxycarbonylmethyl)methyldiphenylphosphonium bromide had m. p. (from acetone) 119—120° (Found: C, 55·65; H, 5·5. $C_{17}H_{20}BrO_2P$ requires C, 55·6; H, 5·45%). Addition of alkali to an aqueous solution of the phosphonium salt at 0° gave a transient precipitate. Chloroform-extraction of the resulting solution gave methyldiphenylphosphine oxide, m. p. and mixed m. p. 113—114°.

Phosphonium Salts Derived from Dimethylphenylphosphine.—Benzyldimethylphenylphosphonium bromide had m. p. 158° (Found: C, 58·5; H, 6·0. $C_{15}H_{18}BrP$ requires C, 58·25; H, 6·0%).

Acetonyldimethylphenylphosphonium chloride had m. p. (from acetone) 107—108° (Found: C, 57·1; H, 6·9. $C_{11}H_{16}ClOP$ requires C, 57·2; H, 6·95%). Addition of alkali to an aqueous solution of the quaternary salt at 0° gave dimethylphenylphosphine oxide, m. p. 117—118°.

(Ethoxycarbonylmethyl)dimethylphenylphosphonium bromide had m. p. (from acetone–benzene) 124—125° (Found: C, 46·8; H, 5·8. $C_{12}H_{18}BrO_2P$ requires C, 47·2; H, 5·9%).

Phenacyldimethylphenylphosphonium bromide had m. p. (from chloroform–benzene) 177—178° (Found: C, 56·7; H, 5·1. $C_{16}H_{18}BrOP$ requires C, 57·0; H, 5·35%). A solution of this quaternary salt in chloroform at 0°, shaken with dilute sodium hydroxide, dried, and evaporated, gave *(benzoylmethylene)dimethylphenylphosphorane*, m. p. (from benzene–light petroleum) 126—127° (Found: C, 74·85; H, 6·8. $C_{16}H_{17}OP$ requires C, 75·05; H, 6·5%).

[11] Horner, Hoffmann, and Beck, *Chem. Ber.*, 1958, **91**, 1583.

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(Formylmethyl)dimethylphenylphosphonium chloride did not crystallise.

Phosphonium Salts Derived from Trimethylphosphine.—To a stirred solution of methylmagnesium iodide, prepared from magnesium (16 g.) and methyl iodide (40 ml.) in ether (200 ml.) and cooled in ice–salt, a solution of phosphorus trichloride (14·7 g.) in ether (50 ml.) was added during 3 hr. The resulting solution was stirred for 0·5 hr. at room temperature and then distilled from an oil-bath into a solution of the reacting halide in ether, cooled in ice. The temperature of the oil-bath was slowly raised to 200°, and held there for 1 hr.

Trimethylphenacylphosphonium bromide had m. p. (from ethanol–ether) 205—206° (Found: C, 46·35; H, 5·65. $C_{11}H_{16}BrOP,\frac{1}{2}H_2O$ requires C, 46·5; H, 5·7%). Addition of aqueous alkali at 0° to a solution of the quaternary salt in ethanol gave *(benzoylmethylene)trimethylphosphorane*, 130—131° (Found: C, 67·8; H, 7·75. $C_{11}H_{15}OP$ requires C, 68·0; H, 7·75%).

(Ethoxycarbonylmethyl)trimethylphosphonium bromide, m. p. (from acetone) 160—162°, was very hygroscopic and always had an odour of trimethylphosphine (Found: C, 33·7; H, 6·35. $C_7H_{16}BrO_2P,\frac{1}{2}H_2O$ requires C, 33·3; H, 6·75%).

Acetonyltrimethylphosphonium chloride did not crystallise.

Reaction of Benzylidenephosphoranes with Fluorenone.—To a stirred solution of benzylidenemethyldiphenylphosphorane, prepared from the phosphonium bromide (3·7 g.) and ethereal 1·4N-butyl-lithium (8 ml.) in ether (100 ml.), a solution of fluorenone (1·8 g.) in ether (25 ml.) was slowly added. The resulting suspension was refluxed for 1·5 hr. and filtered. Evaporation of the filtrate, and crystallisation of the residue from ethanol, gave benzylidenefluorene (60%), m. p. and mixed m. p. 75—76°.

In a similar way, benzylidenedimethylphenylphosphorane gave 53%, and benzylidenetrimethylphosphorane gave 42% of benzylidenefluorene.

Reaction of Benzylidenephosphoranes with Cyclohexanone.—To a stirred solution of benzylidenedimethylphenylphosphorane, prepared from the quaternary bromide (7·8 g.) and ethereal 1·3N-butyl-lithium (19·5 ml.) in tetrahydrofuran (120 ml.), a solution of cyclohexanone (2·5 g.) in tetrahydrofuran (25 ml.) was slowly added. The solution was refluxed overnight, solvent removed under reduced pressure, and the residue extracted with a little cold ether. Distillation of the extract gave benzylidenecyclohexane (72%), b. p. 128—130°/14 mm.

Benzylidenetrimethylphosphorane similarly gave an 80% yield of benzylidenecyclohexane.

Reaction of Benzoylmethylenephosphoranes with Benzaldehyde.—A solution of (benzoylmethylene)trimethylphosphorane (2·3 g.) and benzaldehyde (1·26 g.) in benzene (50 ml.) was refluxed for 18 hr., solvent evaporated, and the residue extracted with cold light petroleum. Evaporation of the extract, and crystallisation of the residue from aqueous ethanol, gave benzylideneacetophenone (92%), m. p. 55—56°. The residue from the extraction crystallised from light petroleum to give trimethylphosphine oxide (95%), m. p. 138—140°.

Similarly, (benzoylmethylene)methyldiphenylphosphorane gave benzylideneacetophenone (73%) and methyldiphenylphosphine oxide (95%), m. p. and mixed m. p. 113—114°; (benzoylmethylene)dimethylphenylphosphorane gave benzylideneacetophenone (50%) and dimethylphenylphosphine oxide (50%), m. p. and mixed m. p. 117—118°.

Reaction of Methylenetrimethylphosphorane with Benzophenone.—To a stirred suspension of tetramethylphosphonium iodide (4·4 g.) in ether (150 ml.), ethereal 1·3N-butyl-lithium (17 ml.) was added and the suspension stirred at room temperature for 30 hr. A solution of benzophenone (3·7 g.) in ether (50 ml.) was then slowly added, the ether removed by distillation and replaced by tetrahydrofuran, and the suspension refluxed for 3 days. Evaporation of the tetrahydrofuran, and extraction of the residue with ether, gave an oil which, on distillation, gave a fraction, b. p. 141—143°/12 mm. Traces of benzophenone were removed from this by treatment with Girard reagent " T." The residue of 1,1-diphenylethylene (40%) had an infrared spectrum identical with that of authentic material.

Reaction of Methylenetrimethylphosphorane with Cyclohexanone.—To a stirred suspension of tetramethylphosphonium iodide (7·3 g.) in 2,2′-dimethoxydiethyl ether (120 ml.), ethereal 1·3N-butyl-lithium (26 ml.) was added. After 15 min. the solution became clear. A solution of cyclohexanone (3·3 g.) in 2,2′-dimethoxydiethyl ether (15 ml.) was then added, and the resulting suspension heated at 100° for 20 hr. and distilled through an efficient column under a reflux-ratio head. A fraction of b. p. 95—115° was collected which, on redistillation, gave methylenecyclohexane (0·5 g.), b. p. 104—108°, identified by infrared spectrum and by gas–liquid chromatography.

Reaction of (Ethoxycarbonylmethyl)dimethylphenylphosphonium Bromide with Benzaldehyde

and Pyridine.—A solution of the phosphonium bromide (1·4 g.), benzaldehyde (0·5 g.), and pyridine (1 ml.) in nitromethane (25 ml.) was refluxed for 18 hr., solvent then removed under reduced pressure, and the residue extracted with benzene. The extract was washed several times with water, then evaporated, and the residue was extracted with cold light petroleum to give, on evaporation of the extract, an oil, $\lambda_{max.}$ 275 mμ. Alkaline hydrolysis of this gave cinnamic acid (0·15 g.), m. p. and mixed m. p. 132—133°.

Reaction of (Ethoxycarbonylmethyl)trimethylphosphonium Bromide with Benzaldehyde and Triethylamine.—A suspension of the phosphonium bromide (5 g.) and triethylamine (2·5 g.) in 2,2′-dimethoxydiethyl ether (100 ml.) was stirred at room temperature overnight, benzaldehyde (1·2 g.) added, and the solution heated at 90° for 20 hr. Solvent was then removed under reduced pressure, the residue extracted with cold ether, and the extract distilled. A fraction of b. p. 135—145°/13 mm. was collected. Alkaline hydrolysis of this gave cinnamic acid (0·8 g.), m. p. and mixed m. p. 132—133°.

Reaction of (Ethoxycarbonylmethyl)trimethylphosphonium Bromide with Cyclohexanone and Triethylamine.—A solution of the quaternary bromide (10·3 g.) and triethylamine (5·1 g.) in nitromethane (100 ml.) was stirred at room temperature for 3 hr., cyclohexanone (4·15 g.) added, and the solution refluxed for 24 hr. Solvent was then removed under reduced pressure and the residue extracted with cold ether. The extract was washed with dilute hydrochloric acid and with water, dried, evaporated, and distilled to give cyclohexanone (0·53 g.), b. p. 47°/15 mm., and a fraction (1·3 g.), b. p. 100—115°/15 mm. Alkaline hydrolysis of this fraction gave two crystalline acidic products: a substance (0·15 g.), m. p. (from aqueous ethanol) 122—123°, $\lambda_{max.}$ 226 mμ (ε 11,000 in ethanol), 3·2, 5·68 μ (Found: C, 68·25; H, 8·05%), and cyclohexylideneacetic acid (0·15 g.), m. p. and mixed m. p. 88—89°.

One of us (D. M. W.) acknowledges a maintenance grant from the Department of Scientific and Industrial Research.

THE UNIVERSITY, LEEDS, 2. [*Received, August 9th,* 1960.]

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247. *Studies with Dithizone. Part VII.*[1] *The Action of Halogens on Dithizone and its Analogues.*

By H. IRVING and R. S. RAMAKRISHNA.

Diphenyl-, di-*p*-bromophenyl-, and di-*p*-tolyl-thiocarbazone form sparingly soluble 1 : 1 adducts with iodine which are dissociated into their components on dissolution in chloroform. With iodine *S*-methyldithizone (3-methylthio-1,5-diphenylformazan) gives a non-stoicheiometric adduct with a characteristic spectrum.

The action of bromine on dithizone yields a 1 : 1 adduct of bromine with a monobrominated dithizone, 1(or 5)-*p*-bromophenyl-3-mercapto-5(or 1)-phenylformazan. The values for the wavelengths and intensities of maximum optical absorption of this monobromodithizone (and of its mercury complex) are the mean of those for the unsubstituted and the dibromo-substituted analogues.

The action of chloramine-T upon dithizone yields a yellow oxidation product apparently identical with that obtained by other routes.

3-Bromo(or nitro)-1,5-di-*p*-bromophenylformazan did not react with either iodine or bromine.

DURING a general study of dithizone and its derivatives[1] we have investigated their reactions with the halogens. Jet-black crystals separate when solutions in chloroform of dithizone (3-mercapto-1,5-diphenylformazan; I; Ar = Ar′ = Ph) and iodine are mixed. From an experiment in which the product was treated with aqueous sodium thiosulphate,

[1] Part VI, Irving and Bell, *J.*, 1954, 4253.

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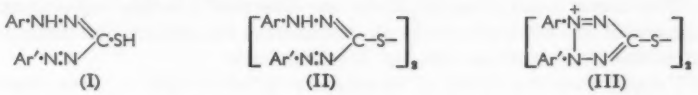
Bamberger, Ormerod, and Padova [2] proposed the empirical formula $C_{13}H_{12}N_4S,I_2$. No further work has been reported.



(I) (II) (III)

Since dithizone can exist in the thiol form (as I) reaction with iodine might be expected to yield the disulphide (II) (or its hydriodide). Moreover, the redox system

$$\text{Formazan} \rightleftharpoons \text{Tetrazolium ion} + H^+ + \text{electron}$$

is also readily set up and it is possible that Bamberger's black substance is the iodide (or more probably, in view of its intense colour, the periodide) of the bistetrazolium ion (III).

We have repeated Bamberger's preparation under various conditions and confirmed the composition of the black substance as $C_{13}H_{12}N_4S,I_2$ by ultimate analysis, by spectrophotometry (see below), and by its reaction with standard sodium thiosulphate solution. Its virtual insolubility in water makes it impossible to test for iodide (or periodide) ions. The solubility in all organic solvents is also low, but the absorption spectrum of an almost saturated solution in chloroform ($1{\cdot}85 \times 10^{-5}$M) closely resembled that of dithizone itself with maxima at 440 and 605 mμ and a minimum at 505 mμ. Whilst this is evidence against the formation of any oxidation product, it is also inconsistent with that of an iodine substitution product of dithizone, for nuclear halogenation is known to produce a bathochromic shift of the whole spectrum (see p. 1275). However, treatment of the black substance was shown to regenerate dithizone, and the molar ratio (dithizone liberated) : (iodine equivalent of the thiosulphate consumed) was always 1 : 1 within the limits of experimental error.

A detailed examination of the absorption spectrum of the black substance showed that, while the ratio $\varepsilon_{605}/\varepsilon_{440} = 2{\cdot}53$ agreed well with the value reported for highly purified dithizone ($2{\cdot}59 \pm 0{\cdot}07$), yet the ratio $\varepsilon_{440}/\varepsilon_{505} = 2{\cdot}39$ was below Cooper and Sullivan's value [3] of $2{\cdot}66 \pm 0{\cdot}06$, thus indicating the presence of a second component with an absorption maximum near 505 mμ. This is precisely the wavelength at which solutions of iodine in chloroform exhibit strong absorption. On the assumption that Bamberger's substance is simply a 1 : 1 adduct which is dissociated completely into iodine and dithizone when dissolved in chloroform, proved possible to reproduce the experimental absorption spectrum (Fig. 1) from the known absorption spectra of iodine and dithizone, the greatest deviation throughout the range 410—620 mμ being ±3%. Since the molecular extinction coefficient of iodine is so much less than that of dithizone even at 505 mμ ($10^{-3}\varepsilon$ 0·92 and $6{\cdot}0 \pm 0{\cdot}1$ respectively) where the absorption of the latter is at a minimum, the iodine never contributes more than 15% to the total absorbancy and the precision of the optical measurements is insufficient to determine the degree of dissociation of the iodine–dithizone adduct as a function of its concentration in solution.

Similar 1 : 1 adducts are formed as black crystalline precipitates, very sparingly soluble in carbon tetrachloride, when solutions of iodine and di-*p*-bromophenyl- or di-*p*-tolylthiocarbazone (as I) in chloroform are mixed. The absorption spectra of these adducts (not reproduced) were indistinguishable from those constructed for equimolecular mixtures of the components.

The interaction of solutions in chloroform of *S*-methyldithizone [1] (3-methylthio-1,5-diphenylformazan) and iodine yielded fine, needle-shaped, black crystals with a metallic reflex. Although almost insoluble in carbon tetrachloride they dissolved in a 5 : 1 mixture of chloroform and ether to give a solution whose absorption spectrum showed maxima at 296 mμ (ε 13,200) and 365 mμ (ε 8100) with a minimum at 329 mμ (ε 4500). When

[2] Bamberger, Ormerod, and Padova, *Annalen*, 1925, **446**, 260.
[3] Cooper and Sullivan, *Analyt. Chem.*, 1951, **23**, 613.

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the organic phase was shaken with an aqueous solution of sodium thiosulphate, its absorption spectrum reverted to that of *S*-methyldithizone ($\lambda_{max.}$ 418 and 545 mμ, $\lambda_{min.}$ 500 and 348 mμ). The molar ratio (*S*-methyldithizone liberated) : (iodine equivalent of thiosulphate consumed) was not the same for all specimens of this adduct, and ultimate analysis also indicated that is composition was not stoicheiometric.

Fischer [4] noted that the action of bromine on dithizone gave a crystalline product " with a magnificent metallic reflex " but he carried out no analyses or further investigation. We observed that the addition of bromine to a green solution of dithizone in chloroform

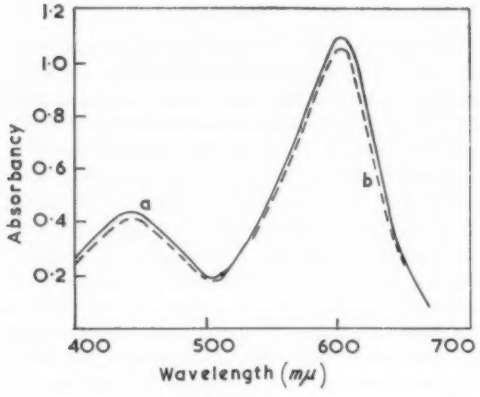


FIG. 1. (a) *Solid line: Absorption spectrum in chloroform of the adduct of dithizone and iodine,* $2{\cdot}5098 \times 10^{-5}$ *mole/l.* (b) *Broken line: Absorption spectrum calculated for equimolecular mixture of iodine and dithizone, each* $2{\cdot}5098 \times 10^{-5}$ M, *from known molecular extinction coefficients of dithizone* [3] *and iodine.*

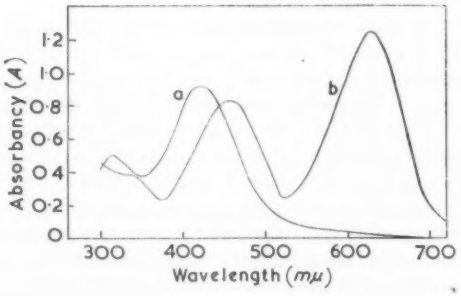


FIG. 2. (a) *Absorption spectrum in carbon tetrachloride of the product of the action of bromine on dithizone.* (b) *Absorption spectrum in carbon tetrachloride of the crude bromination product after having been kept over sodium thiosulphate.*

first quickly changed the colour to violet and that green crystals with a pronounced copper reflex soon separated. The yield of the final product and its nature did not appear to vary greatly with the ratio [dithizone] : [bromine] provided more than two equivalents were employed. The crude adduct dissolved in chloroform to give a greenish-yellow solution with absorption maxima at 428—430 mμ (principal) and 615 mμ (subsidiary): those of dithizone itself are at 440 and 605 mμ in this solvent. On storage at room temperature, and more quickly in the presence of solid sodium thiosulphate, the colour became definitely more green, the absorption peak at the shorter wavelength shifted to 450 mμ and the absorption at the longer wavelength became greater than that at 450 mμ. Similar behaviour was observed in carbon tetrachloride save that there was now a single absorption band at 420 mμ in the original solution (Fig. 2, curve *a*) which shifted to 458 mμ as a new maximum of greater intensity appeared at 628 mμ (Fig. 2, curve *b*).

The crude bromination product was not acidic, for it could not be extracted from its solution in chloroform or carbon tetrachloride by shaking with aqueous ammonia. On

[4] Fischer, *Annalen*, 1882, **212**, 316.

the other hand, the dark green substance obtained by treating an organic solution of the crude bromination product with aqueous sodium thiosulphate could be extracted by aqueous ammonia or sodium hydroxide in which it formed an orange solution. When this was acidified a black precipitate was formed which dissolved in chloroform or carbon tetrachloride to give a deep green solution. This behaviour is typical of that of dithizone and its homologues. A sample was purified by successive extractions by 1 : 100 isopiestic ammonia [5] and reversion by 1 : 100 isopiestic hydrochloric acid into purified organic solvent. The bromination product was finally obtained as a bluish-black solid, m. p. 148—150° (decomp.). Ultimate analysis indicated that it was a monobromo-substitution product of dithizone. The location of the bromine atom in the *para*-position of one of the benzene rings was established by reduction with stannous chloride and the isolation of *p*-bromoaniline. The absorption spectra of the new mono-*p*-bromodithizone [1(or 5)-*p*-bromophenyl-3-mercapto-5(or 1)-phenylformazan; (I) Ar = Ph, Ar′ = *p*-Br·C_6H_4] closely resembled that of dithizone and synthetic di-*p*-bromophenylthiocarbazone (I; Ar = Ar′ = *p*-Br·C_6H_4), but the position of the absorption maxima lay between those

TABLE 1. *Absorption spectra of substituted dithizones in carbon tetrachloride.*

Formulæ as I		Dithizone				Mercury complex	
Ar	Ar′	$\lambda_{max.}$	$10^{-3}\varepsilon$	$\lambda_{min.}$	$\lambda_{max.}$	$\lambda_{max.}$	$10^{-3}\varepsilon$
Ph	Ph	620 [a]	34·6 ± 0·84 [a]	515	450	490 [a]	70 [a]
p-Br·C_6H_4	Ph	628	34·4	520	458	496	76·5
p-Br·C_6H_4	*p*-Br·C_6H_4	635	31·3	526	464	502	71·5

[a] Ref. 3.

of the unsubstituted parent and the disubstituted analogue (Fig. 3). The molecular extinction coefficients of the monobrominated dithizone and of its mercuric complex were determined [6] from measurements of the absorbancy at 628 mμ ($\lambda_{max.}$ for the reagent) and 496 mμ ($\lambda_{max.}$ for the mercuric complex) of solutions obtained by equilibrating solutions of the monobromodithizone in carbon tetrachloride with N/4-sulphuric acid containing varying known amounts of mercuric ion (Fig. 4). The results of similar experiments with dithizone and with synthetic di-*p*-bromophenylthiocarbazone [7] are given in Table 1. Pupko and Pel'kis have previously noted [8] that " the values for the absorption maxima of unsymmetrical thiocarbazones are equal to the arithmetic mean of the maxima for the two corresponding symmetrical thiocarbazones," although it must be pointed out that, in our experience, too much reliability cannot be placed on the actual values they quote.

The absorption spectrum of monobromodithizone obtained by direct bromination of dithizone was shown to be indistinguishable from that of the thiocarbazone produced by reduction with ammonium sulphide of 5(or 1)-*p*-bromophenyl-3-nitro-1(or 5)-phenylformazan, itself obtained by coupling nitroformaldehyde phenylhydrazone, Ph·NH·N:CH·NO_2, with diazotised *p*-bromoaniline.

The nature of the initial bromination product of dithizone was then investigated by adding increasing amounts of bromine to a solution of pure monobromodithizone in carbon tetrachloride. The absorption at 628 mμ decreased and became negligible when an excess of bromine had been added: simultaneously the absorption at 420 mμ increased to a maximum value as the composition approached that represented in Fig. 2, curve *a*. From the changes in optical absorbancy (Fig. 5) the formation of a 1 : 1 adduct, $C_{13}H_{11}N_4BrS,Br_2$, was established. Since this adduct does not absorb at 628 mμ, the absorbancy of mixtures of bromine and the monobromodithizone at this wavelength will constitute a measure of the concentration of uncombined monobromodithizone. From this value and that of the

[5] Irving and Cox, *Analyst*, 1958, **83**, 526.
[6] Irving and Bell, *J.*, 1953, 3538.
[7] Irving and Hale, unpublished work.
[8] Pupko and Pel'kis, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 1623.

known ratio $\varepsilon_{628}/\varepsilon_{420}$ for the pure substance, the absorbancy due to uncombined monobromodithizone at 420 mμ can be calculated. Since the absorbancy due to bromine at this wavelength is negligible ($\varepsilon \sim 215$), that due to the adduct alone can be calculated and correlated with the amount of monobromodithizone initially present. From the known stoicheiometry of the adduct the value of the molecular extinction coefficient is found to be $10^{-3}\varepsilon_{420} = 26{\cdot}9$. When bromine was added to a solution of monobromodithizone in chloroform the absorbancy at 615 mμ was not reduced to zero even when a slight excess of bromine had been added over that required to form the adduct,

FIG. 3. *Absorption spectra in carbon tetrachloride of* (a) *diphenylthiocarbazone,* (b) *p-bromophenylphenylthiocarbazone, and* (c) *di-p-bromophenylthiocarbazone, all of concentration* $\sim 3 \times 10^{-5}$M.

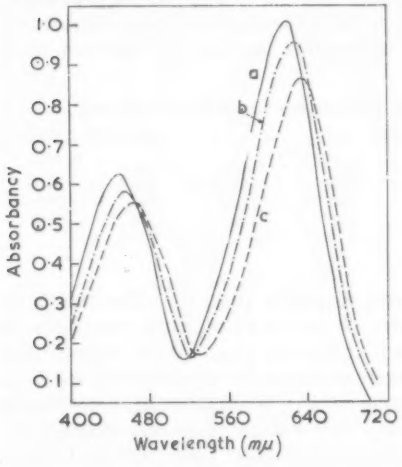
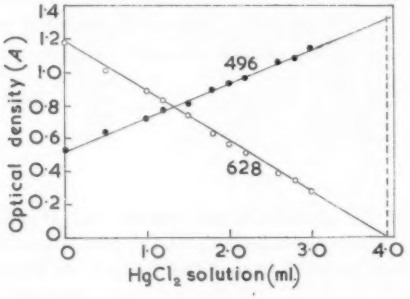


FIG. 4. *Determination of the molar extinction coefficient of monobromodithizone in carbon tetrachloride by titration with mercuric ions. (The figures on the plots are the relevant wavelengths in mμ.)*



$C_{13}H_{11}N_4BrS,Br_2$, which suggests that it is more readily dissociated in chloroform than in carbon tetrachloride.

The action of bromine on a specimen of synthetic di-*p*-bromophenylthiocarbazone also gave a 1 : 1 adduct as a black solid, m. p. 167°, with an absorption maximum at 426 mμ (in CCl_4) and a small peak at 635 mμ. On treatment with aqueous sodium thiosulphate the spectrum reverted to that of the original dibromodithizone ($\lambda_{max.}$ 464, 635 mμ). The formula of the adduct was shown spectrophotometrically to be $C_{13}H_{10}N_4Br_2S,Br_2$ by the method used previously for the adduct with monobromodithizone (cf. Fig. 5), and the molecular extinction coefficient was found to be somewhat lower with $10^{-3}\varepsilon_{426} = 25{\cdot}2$.

The addition of bromine to a solution of di-*p*-tolylthiocarbazone (I; Ar = Ar′ = *p*-C_6H_4Me) in chloroform changed the colour at once from green to violet, but no crystalline product could be obtained on cooling or concentrating the solution. The spectra of mixtures of bromine and di-*p*-tolylthiocarbazone recorded on a Unicam S.P. 700 instrument were not reproducible and reverted rather quickly to that of the parent dithizone. Clearly, no stable adduct is formed and no definite compound could be isolated from the action of bromine on *S*-methyldithizone.

The action of elementary chlorine upon dithizone would be expected to lead to extensive decomposition, and even treatment with chloramine-T was found to yield a product which could not be reconverted into dithizone on treatment with reducing agents such as hydroxylamine, sodium hydrogen sulphite, or sodium thiosulphate. Under carefully controlled conditions the action of chloramine-T on dithizone is to produce a yellow substance with

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a single absorption maximum in the visible region at 410 mμ (ε 8854) which suggests (Table 2) that it may be the yellow oxidation product noted by previous workers although its actual structure is still in doubt.

TABLE 2. *Oxidation products of dithizone.*

Oxidant used	$\lambda_{max.}$	$\varepsilon_{max.}$	Ref.
Chloramine-T	410	8854	Present work
Dil. HNO_3; H_2O_2	410	9150	9
$[Ph_2I]^+$	410	9130	10
Air	410	8800	11

A spectrophotometric study of the addition of bromine and iodine to 3-bromo(or nitro)-1,5-di-*p*-bromophenylformazan (as I; Br or NO_2 for SH) showed no evidence of the formation of an adduct, suggesting that this requires the presence of a sulphur atom.

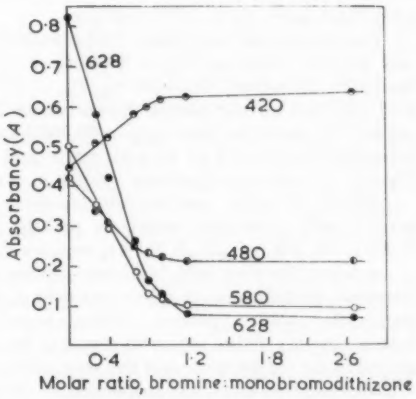

FIG. 5. *Determination of the composition of the adduct of bromine and monobromodithizone by Harvey and Manning's method:*[15] *variation in absorbancies of solutions of monobromodithizone and bromine with the mole ratio of the components. (The figures on the plots are the relevant wavelengths in* mμ.)

EXPERIMENTAL

Glassware used in handling solutions of dithizones or their derivatives was scrupulously freed from traces of metals and oxidising impurities by methods described elsewhere.[12] Organic solvents were purified by standard methods and redistilled before use.[12] Metal-free solutions of ammonia and of hydrochloric acid were prepared by isopiestic distillation.[5]

Spectrophotometric measurements were made at room temperature with a Unicam S.P. 500 instrument or recorded with a Unicam S.P. 700 instrument with matched silica cells.

Adduct of Iodine and Dithizone.—A solution of iodine (0·4 g.) in warm chloroform (20 ml.) was added to one of dithizone (0·4 g.) in chloroform (20 ml.) at 50°. The colour of the solution changed from green to violet-blue, and violet-black crystals with a metallic lustre (0·5 g.), m. p. 128°, were deposited (Found: C, 30·9; H, 2·7; N, 11·1. $C_{13}H_{12}I_2N_4S$ requires C, 30·6; H, 2·4; N, 11·0%). The iodine content was determined by dissolving 28·0 mg. in 100 ml. of pure chloroform, equilibrating this with 25·0 ml. of 0·09745N-sodium thiosulphate, and titrating the aqueous phase with standard iodine solution (Found: I, 47·7. $C_{13}H_{12}I_2N_4S$ requires I, 49·8%). From the absorbancy at 605 mμ of a solution in chloroform (12·8 mg./l.) which corresponds to a concentration of 6·7 mg./l. of free dithizone and thence to a molar ratio dithizone : iodine of 1 : 0·96. The composition of the *adduct* was confirmed by a titrimetric determination of iodine by means of sodium thiosulphate.

*Adduct of Iodine and Di-*p*-bromophenylthiocarbazone.*—Solutions of freshly purified di-*p*-bromophenylthiocarbazone (0·37 g.) in chloroform (50 ml.) and iodine (0·27 g.) in chloroform

[9] Weber, Diss., Zagreb, 1956.
[10] Irving and Cox, unpublished work.
[11] (*a*) Fischer and Weyl, *Wiss. Veroff. Siemens Werken*, 1935, **14**, 41; (*b*) Liebhafsky and Winslow, *J. Amer. Chem. Soc.*, 1937, **59**, 1966.
[12] (*a*) Irving, Andrews, and Risdon, *J.*, 1949, 541; (*b*) Irving and Butler, *Analyst*, 1953, **78**, 571.

(50 ml.) were mixed as above. The solution became violet-green, and greenish-yellow crystals (0·3 g.), m. p. 132°, with a metallic lustre separated. The absorption spectrum in chloroform showed maxima at 625 and 456 mμ with a minimum at 520 mμ. The peak ratio $\varepsilon_{625}/\varepsilon_{456} = 2{\cdot}42$ agreed with that reported for pure di-*p*-bromophenylthiocarbazone,[13] but the ratio $\varepsilon_{456}/\varepsilon_{520} = 2{\cdot}32$ was much lower than that for the pure thiocarbazone (2·54), indicating the presence of a second component absorbing near 520 mμ. The absorbancy (1·219) at 625 mμ of a solution of this adduct in chloroform (17·9 mg./l.) corresponds to a concentration of 11·34 mg./l. of di-*p*-bromophenylthiocarbazone and thence to a molar ratio of thiocarbazone : iodine = 1 : 0·964. The composition was confirmed by a titrimetric determination of iodine.

*Adduct of Iodine and Di-*p*-tolylthiocarbazone.*—A laboratory sample [13] of di-*p*-tolylthiocarbazone (1 g.) in carbon tetrachloride was purified by Cowling and Miller's method.[14] The organic extract of the purified reagent was evaporated to dryness under suction in a vessel protected from the light. Iodine (0·3 g.) in chloroform (20 ml.) was added slowly to a solution of the pure ditolylthiocarbazone (0·3 g.; m. p. 130°) in chloroform (20 ml.) at 50°. The colour changed from green to brownish-violet, and after being cooled in ice the adduct separated as a jet-black solid, m. p. 122° (0·41 g.).

The absorption spectrum of the adduct in chloroform (11·8 mg./l.) had maxima at 615 and 451 mμ (ratio $\varepsilon_{615}/\varepsilon_{451} = 3{\cdot}53$) close to that for the pure reagent (3·70) as reported by Morris.[13] However, the ratio $\varepsilon_{451}/\varepsilon_{509} = 1{\cdot}68$ was definitely lower than the value $\varepsilon_{453}/\varepsilon_{510} = 2{\cdot}12$ reported for the parent thiocarbazone.[13] From the measured absorbancy (1·165) at 615 mμ and by using the value $\varepsilon_{615} = 56{,}000$ found by Morris,[13] the concentration of di-*p*-tolylthiocarbazone was found to be 5·91 mg./l. and the molar ratio thiocarbazone : iodine = 1 : 1·11. The adduct was very sparingly soluble in carbon tetrachloride.

Adduct of Iodine and S-*Methyldithizone.*—Prepared as above, this *adduct* formed black needles with a metallic lustre, m. p. 118° (Found: C, 26·6; H, 2·6. $C_{14}H_{14}N_4S,I_2$ requires C, 32·1; H, 2·9. $C_{14}H_{14}N_4S,1{\cdot}4I_2$ requires C, 26·8; H, 2·2%).

Action of Bromine with Dithizone.—When bromine (3·52 g.) in chloroform (30 ml.) was added dropwise to dithizone (2 g.) in chloroform (100 ml.), cooled in ice and constantly stirred, a deep violet colour appeared. When about half the bromine had been added a greenish solid with a coppery reflex began to separate on the walls of the vessel. The solution was finally placed in ice for 20 min., and the solid adduct collected (yield 2·23 g.; m. p. 110°).

The crude product was suspended in chloroform (25 ml.) and shaken with successive small amounts of 10% aqueous sodium hydrogen carbonate until the aqueous phase was neutral to litmus. The organic phase was then shaken with successive 100 ml. portions of 20% sodium thiosulphate solution until a test portion when shaken with water no longer gave a colour with potassium iodide and starch. The organic phase was finally well washed with water and taken to dryness under reduced pressure, crude monobromodithizone remaining as an almost black solid, m. p. 150° (1·65 g.). For further purification the crude product (1 g.) was treated by Cowling and Miller's procedure,[14] in which metal-free acid and alkali are used [5] and the final organic phase is evaporated slowly to dryness under reduced pressure and in the dark. 1(or 5)-p-*Bromophenyl*-3-*mercapto*-5(or 1)-*phenylformazan* separated from chloroform as almost black crystals with a metallic reflex, m. p. 152—155° (decomp.) (Found: C, 46·4; H, 3·4. $C_{13}H_{11}BrN_4S$ requires C, 46·6; H, 3·3%). The spectrum was identical with that of an authentic specimen prepared.

Crude bromination product from 2 g. of dithizone was treated with sodium thiosulphate to remove excess of bromine, then dissolved in glacial acetic acid and heated under reflux with concentrated hydrochloric acid and stannous chloride until the solution was completely colourless (3 hr.). The mixture was made strongly alkaline with sodium hydroxide and distilled in steam. A white solid which separated in the first 25 ml. of the distillate was identified as *p*-bromoaniline by its infrared spectrum in carbon disulphide, and by the formation of *p*-bromoacetanilide (m. p. and mixed m. p. 166—167°).

Spectrophotometric Determination of the Composition of the Adduct of Bromine and Monobromodithizone.—Solutions in carbon tetrachloride of purified monobromodithizone (5 ml., approx. $2{\cdot}4 \times 10^{-5}$M) and bromine (x ml. of $3{\cdot}1864 \times 10^{-4}$M) were mixed with $(5 - x)$ ml. of pure solvent, and their absorbancies measured at 420 and 628 mμ. The results plotted in Fig. 5 indicate a molecular ratio $C_{13}H_{11}BrN_4S : Br_2$ of 1 : 0·93.

[13] Morris, B.Sc. Thesis, Oxford, 1959.
[14] Cowling and Miller, *Ind. Eng. Chem. Analyst.*, 1941, **13**, 145.

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Determination of the Molecular Extinction Coefficient of Monobromodithizone by Titration with Mercuric Ions.—A solution of monobromodithizone in carbon tetrachloride was purified by Cowling and Miller's method.[14] Aliquot portions (5 ml.) were equilibrated with x ml. of a $2{\cdot}19 \times 10^{-5}$M-solution of mercuric chloride in N/4-sulphuric acid and $(5 - x)$ ml. of N/4-sulphuric acid by being shaken mechanically in stoppered Pyrex tubes for 10 min. The organic phase was then separated, and its absorbancy measured at 496 and 628 mμ. The results are plotted in Fig. 4 and lead to the values given in Table 1 for the molecular extinction coefficient of monobromodithizone and its mercury complex (which is assumed to be a stoicheiometric 1 : 2 complex as has been demonstrated for dithizone itself [12a]).

Determination of the Molecular Extinction Coefficient of the Adduct of Bromine and Monobromodithizone.—Mixtures of $(5 - x)$ ml. of carbon tetrachloride with x ml. of a solution of bromine ($3{\cdot}1864 \times 10^{-4}$M) and 5 ml. of approx. $2{\cdot}4 \times 10^{-5}$M-monobromodithizone in carbon tetrachloride were prepared, and their absorbancies measured at 628 and 420 mμ. The results are shown in columns 1—3 and 6—8 of the following Table. The absorbancy, A_{420}*, due to

x	A_{628}	A_{420}	A_{420} *	A_{420} (adduct only)	x	A_{628}	A_{420}	A_{420} *	A_{420} (adduct only)
0	0·823	0·445	0·445	0	0·60	0·160	0·595	0·087	0·508
0·20	0·578	0·506	0·313	0·193	0·70	0·126	0·615	0·068	0·547
0·30	0·434	0·514	0·235	0·279	0·90	0·079	0·620	0·043	0·577
0·50	0·250	0·580	0·135	0·445	2·00	0·068	0·630	0·037	0·593

uncombined monobromodithizone was then calculated from A_{628} and the experimentally determined ratio $\varepsilon_{420}/\varepsilon_{628} = 0{\cdot}5407$ for the pure thiocarbazone and thence the contribution due to the adduct alone (columns 5 and 10). A plot of A_{628} for the thiocarbazone against A_{420} for the adduct (not reproduced) was a straight line of slope 1·274. Since $\varepsilon_{628} = 34{,}390$ for pure monobromodithizone in carbon tetrachloride, the molecular extinction coefficient of its bromine adduct is $\varepsilon_{420} = 34{,}390/1{\cdot}274 = 26{,}900$.

*Adduct of Bromine and Di-*p*-bromophenylthiocarbazone.*—Prepared from a solution of the components as in the case of the adduct of monobromodithizone, this formed a black crystalline solid, m. p. 168°. Its stoicheiometry was determined similarly by Harvey and Manning's method.[15] Its molecular extinction coefficient was calculated from the absorbancies of mixtures of dibromodithizone (5 ml. of approx. $2{\cdot}7 \times 10^{-5}$M), bromine (x ml. of $1{\cdot}8069 \times 10^{-4}$M), and of carbon tetrachloride $(5 - x)$ ml. The absorbancy due to the adduct alone was calculated as before from the following results:

x	A_{635}	A_{426}	A_{426} *	A_{426} (adduct only)	x	A_{635}	A_{426}	A_{426} *	A_{426} (adduct only)
0	0·863	0·390	0·390	0·0	1·20	0·297	0·610	0·134	0·476
0·20	0·770	0·434	0·348	0·086	1·50	0·146	0·662	0·066	0·596
0·60	0·590	0·491	0·267	0·224	2·00	0·054	0·668	0·024	0·644
0·80	0·516	0·532	0·233	0·299					

From the slope (1·240) of the linear plot of A_{635} against A_{426} (adduct alone) and the value $\varepsilon_{635} = 31{,}360$ for the purified dibromodithizone we calculate ε_{426}(adduct) = 25,290.

*Action of Chloramine-*T *upon Dithizone.*—When 20 ml. of a solution of dithizone in carbon tetrachloride ($3{\cdot}919 \times 10^{-5}$M) were shaken in a 100 ml. Pyrex separating funnel with chloramine-T (2·6 mg., a factitious excess) in water (20 ml.), the green colour rapidly faded to yellow. After 2 min. the organic phase was withdrawn and its spectrum recorded with a Unicam S.P. 700 instrument. A single absorption band was observed in the visible region at 410 mμ. From the absorbance of 0·347 (1 cm. cell) the molecular extinction coefficient is $\varepsilon_{410} = 8854$.

We are indebted to G. F. Watts and F. Hale for the preparation of samples of substituted dithizones, and to J. M. Crewe for preliminary measurements. One of us (R. S. R.) gratefully acknowledges facilities for study leave provided by the Council of the University of Ceylon. Grateful acknowledgment is made to the Royal Society for the loan of a recording spectrophotometer.

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[*Received, August 22nd,* 1960.]

[15] Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

248. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part VI.*[1] 1,12:2,3:4,5:6,7:8,9:10,11-*Hexabenzocoronene.*

By J. Monteath Robertson and James Trotter.

Crystals of hexabenzocoronene are monoclinic, with two molecules in a unit cell of dimensions $a = 18{\cdot}42$, $b = 5{\cdot}11$, $c = 12{\cdot}86$ Å, $\beta = 112{\cdot}5°$, space group $P2_1/a$. All the crystals examined have been twinned on (001). The structure has been determined from normal and generalised projections along the b-axis. The carbon skeleton of the molecule is completely planar, but some of the hydrogen atoms are possibly displaced from the aromatic plane. Details of the molecular dimensions and of the intermolecular separations have been obtained.

A detailed X-ray investigation of the crystal and molecular structure of 1,12:2,3:4,5:6,7:8,9:10,11-hexabenzocoronene (I) has been undertaken to obtain an account of the dimensions of the molecule. The extreme stability of this hydrocarbon is indicated by its very high melting point. Unfortunately all the crystals available for examination were twinned and gave rather poor X-ray photographic records, so that, although partial three-dimensional data have been used to give an independent estimate of all three positional parameters for each carbon atom, the accuracy of the results is rather limited.

Experimental

Crystals of hexabenzocoronene, obtained by crystallisation from boiling pyrene, followed by sublimation in a high vacuum, were yellow needles elongated along the b-axis. The density, unit-cell dimensions, and space group were determined as recorded in Part V.[1] The several crystals examined were twinned on (001), and no single crystal could be obtained. It was not too difficult however to interpret and index the films, and the analysis proceeded satisfactorily with the data collected using the twinned crystals. The crystal data were: 1,12:2,3:4,5:6,7:8,9:10,11-hexabenzocoronene, $C_{42}H_{18}$; M, 522·6; m. p. >700°. Monoclinic, $a = 18{\cdot}42 \pm 0{\cdot}05$, $b = 5{\cdot}11 \pm 0{\cdot}01$, $c = 12{\cdot}86 \pm 0{\cdot}03$ Å, $\beta = 112{\cdot}5° \pm 0{\cdot}3°$. Volume of the unit cell = 1118·2 Å^3. d calc. (with $Z = 2$) = 1·542, measured = 1·544 g. cm.$^{-3}$. Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 8{\cdot}13$ cm.$^{-1}$. Total number of electrons per unit cell = $F(000) = 540$. Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd. Space group is uniquely determined as C_{2h}^5–$P2_1/a$.

(I)

The intensities of the $h0l$ and $h1l$ reflexions were recorded on Weissenberg films for a crystal rotating about the b-axis, with Cu-K_α radiation, the equi-inclination method being used for the $h1l$ layer. The multiple-film technique [2] was used to correlate strong and weak reflexions. The range of intensities measured was about 3000 to 1 for the $h0l$ reflexions and 2000 to 1 for the $h1l$ reflexions, the estimates being made visually. On the $h0l$ zone photographs there were only a few cases where reflexions from different parts of the twinned crystal overlapped, so that indexing and intensity estimation were straightforward for most of the reflexions. In addition it was possible, by measuring intensities of reflexions from both parts of the twin, to obtain reliable values for the intensities even for those cases where overlap occurred. On the $h1l$ zone films, since reflexions with h both even and odd were present, indexing was a little more difficult, but reliable estimates of the intensities were obtained for most of the reflexions. There were, however, a few $h1l$ reflexions for which it was considered that either the indexing or intensities might not be reliable, and these were omitted from the $h1l$ zone refinement. These reflexions were all very weak.

The cross-section of the crystal normal to the b-axis was 0·14 × 0·09 mm., and no absorption corrections were applied. The structure amplitudes were derived by the usual formulæ for a mosaic crystal, the absolute scale being established later by correlation with the calculated

[1] Part V, *J.*, 1961, 1115.
[2] Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

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structure factors. 106 independent *h*0*l* reflexions and 99 *h*1*l* reflexions were observed representing 37% and 18% respectively of the possible number observable under the experimental conditions.

TABLE 1. *Final positional and temperature parameters, and deviations* (Δ) *from the mean plane.*

Atom	*x*	*y*	*z*	*X'*	*Y*	*Z'*	*B* (Å²)	Δ (Å)
C 1	0·0389	−0·178	0·4053	0·662	−0·910	4·938	4·2	+0·065
2	0·0965	0·002	0·4773	1·642	0·010	5·458	4·2	+0·019
3	0·1289	0·172	0·4221	2·194	0·879	4·520	4·2	+0·008
4	−0·1379	−0·690	0·2093	−2·347	−3·526	3·664	4·2	−0·002
5	−0·0794	−0·513	0·2739	−1·351	−2·621	4·082	4·2	−0·006
6	−0·0483	−0·348	0·2198	−0·822	−1·778	3·167	4·2	−0·020
7	0·0097	−0·175	0·2874	0·165	−0·894	3·628	4·2	−0·024
8	0·0467	0·008	0·2387	0·795	0·041	2·740	4·2	−0·035
9	0·1051	0·173	0·3030	1·789	0·884	3·156	4·2	+0·002
10	0·1397	0·350	0·2507	2·377	1·789	2·239	4·2	−0·012
11	0·1976	0·519	0·3159	3·363	2·652	2·670	4·2	+0·003
12	0·2316	0·698	0·2672	3·941	3·567	1·804	4·2	−0·036
13	−0·1636	−0·695	0·0946	−2·784	−3·551	2·370	4·2	−0·025
14	−0·1302	−0·520	0·0342	−2·216	−2·657	1·358	4·2	−0·026
15	−0·0680	−0·344	0·1058	−1·157	−1·758	1·840	4·2	+0·005
16	−0·0374	−0·175	0·0470	−0·636	−0·894	0·868	4·2	−0·017
17	0·0232	0·000	0·1166	0·395	0·000	1·336	4·2	+0·001
18	0·0582	0·169	0·0675	0·990	0·864	0·458	4·2	+0·012
19	0·1159	0·343	0·1331	1·972	1·753	0·895	4·2	+0·005
20	0·1519	0·516	0·0832	2·585	2·637	−0·001	4·2	+0·019
21	0·2072	0·697	0·1451	3·526	3·562	0·405	4·2	−0·035
Molecular centre	0	0	0	0	0	0	—	0

TABLE 2. *Orientation of the molecule in the crystal.*

$\chi_L = 48° 42'$	$\chi_M = 73° 15'$	$\chi_N = 134° 36'$
$\psi_L = 43° 18'$	$\psi_M = 89° 54'$	$\psi_N = 47° 03'$
$\omega_L = 100° 46'$	$\omega_M = 16° 44'$	$\omega_N = 78° 05'$

Structure Analysis.—[010] *Projection.* The cell dimensions, although greater, are strikingly similar to those found in the coronene structure,[3] and the general arrangement of the molecules is likely to be similar. It was therefore decided to approach the complete solution by a preliminary study of the short *b* axis projection. There are two molecules of hexabenzocoronene in the unit cell and the space group is $P2_1/a$, so that the molecules must be centrosymmetrical and situated on the centres of symmetry at (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,0). In addition it seemed likely that the molecule might conform, at least approximately, to the much higher symmetry 6/*mmm*, so that the whole structure could be established by locating, on the *h*0*l* weighted reciprocal lattice, regions of high intensity corresponding to the 1·2 Å and 2·1 Å spacings of the regular aromatic hexagons. The orientation of the whole molecule was thus easily established from the following outstanding reflexions: (i) corresponding to 1·2 Å spacings, (22,0,$\bar{4}$), (22,0,$\bar{5}$), (10,0,6), (10,0,7), (807), (12,0,$\bar{1}\bar{0}$), (12,0,$\bar{1}\bar{1}$), (14,0,$\bar{1}\bar{1}$); (ii) corresponding to 2·1 Å spacings, (005), (006), (20$\bar{6}$), (10,0,0), (10,0,1), (12,0,0), (10,0,$\bar{5}$), (12,0,$\bar{5}$), (12,0,$\bar{6}$).

Structure factors were calculated for all the observed *h*0*l* reflexions, by using the scattering curve for carbon of Berghuis *et al.*,[4] corrected for thermal vibration with $B = 4·2$ Å² for all the atoms. The discrepancy between measured and calculated structure factors was 24·1%. Refinement of the structure proceeded by computing successive difference syntheses, with (F_o–F_c) as coefficients, and shifting the atoms to minimise the slopes at the atomic centres. No significant changes in temperature parameters were indicated, and *B* was retained at 4·2 Å² for all the atoms. After three cycles the discrepancy factor had been reduced to 13·1%, and a final (F_o–F_c) synthesis indicated no further changes in positional or temperature parameters. Measured and calculated structure factors are listed in Table 3, and a final F_o synthesis, computed with measured structure amplitudes and calculated signs, is shown in Fig. 1.

y-Co-ordinates. No resolution of the individual atoms in the molecule could be expected in projections down the *a*- or *c*-crystal axes, and the problem of finding the *y*-co-ordinates was

[3] Robertson and White, *J.*, 1945, 607.
[4] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

therefore approached by considering the *h*1*l* structure factors. Approximate *y*-parameters were easily deduced from a consideration of the bond lengths projected on (010). Structure

FIG. 1. (a) *Electron-density projection along the b-axis. Contours at intervals of* 1 eÅ^{-2}, *with the one-electron line broken.*
(b) *Projection of the structure on to* (010).

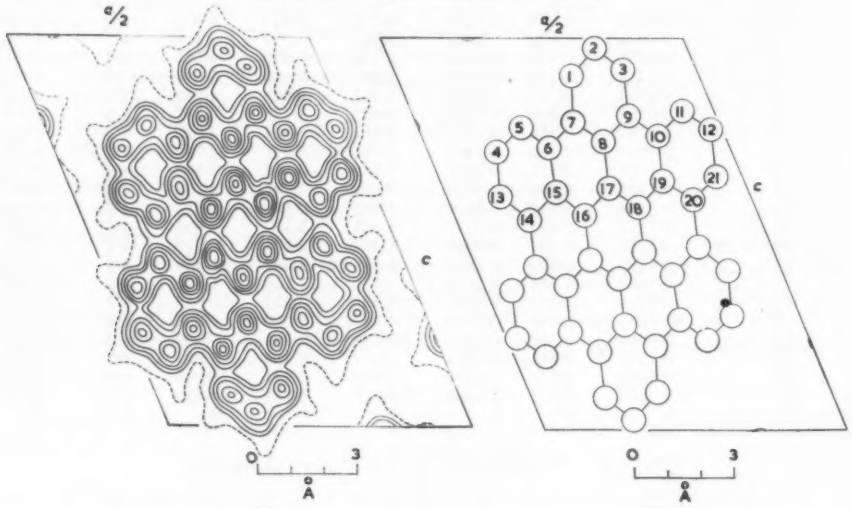
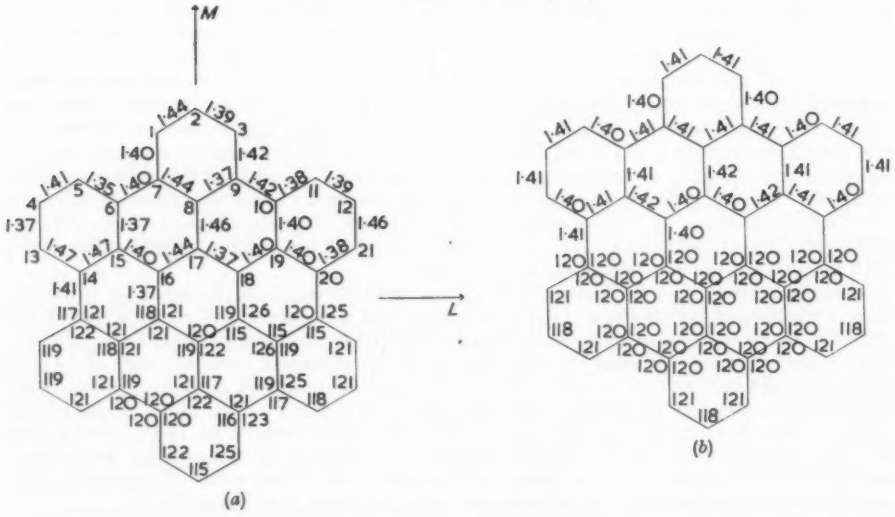


FIG. 2. (a) *Measured bond lengths* (Å) *and valency angles* (*degrees*).
(b) *Mean bond lengths and valency angles.*



factors were calculated for the observed *h*1*l* reflexions, by using these trial *y*-co-ordinates and the *x*, *z*, and *B* parameters from the *h*0*l* refinement. The discrepancy factor was 19·2%. Refinement proceeded by computing cosine and sine difference generalised projections.[5] By this

[5] Rossmann and Shearer, *Acta Cryst.*, 1958, **11**, 829.

method it is possible to refine all three positional parameters x, y, z, and the isotropic temperature parameters, B, simultaneously, but the maps indicated that no significant changes in x, z, and B parameters were required. New y-co-ordinates were obtained, the maximum shift being 0·04 Å, and structure factors were recalculated. The discrepancy factor was 11·7%. A second set of difference generalised projections was calculated, but no further significant changes in y-co-ordinates were indicated. The measured and calculated $h1l$ structure factors are included in Table 3.

Co-ordinates, molecular dimensions, and orientation. The final positional and temperature parameters of the carbon atoms are listed in Table 1, x, y, and z being co-ordinates referred to

FIG. 3. *Normal projection of two parallel molecules.*

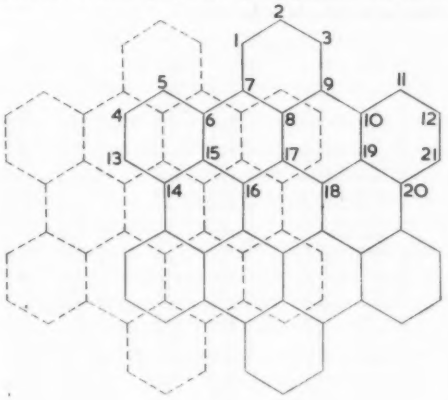
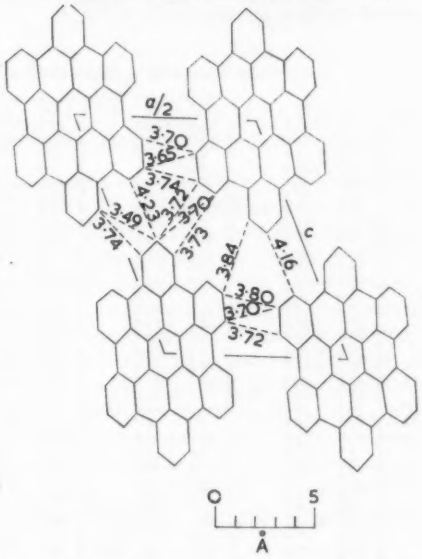


FIG. 4. *Projection of the structure on to* (010), *showing the shorter intermolecular distances.*



the monoclinic crystal axes and expressed as fractions of the unit-cell edges, and X', Y and Z' co-ordinates in Ångström units referred to orthogonal axes a', b, and c.

The equation of the mean molecular plane is

$$0{\cdot}7022X' - 0{\cdot}6814Y - 0{\cdot}2065Z' = 0$$

and the deviations of the atoms from this plane are listed in the final column of Table 1.

The bond lengths and valency angles in the molecule, calculated from the co-ordinates of Table 1, are shown in Fig. 2(a). The mean values, assuming symmetry $6/mmm$, are shown in Fig. 2(b).

The orientation of the molecule in the crystal is given in Table 2, where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; and χ_N, ψ_N, ω_N are the angles which the molecular axes L, M [see Fig. 2(a)], and the plane normal N make with the orthogonal axes a', b, and c. L was taken through the molecular centre and the mid-point of bond 14′—20 (for numbering used see Fig. 3), and M through the molecular centre and atom 2. L, M, and N are thus not accurately mutually perpendicular, the angles being $L \wedge M = 89° 17'$, $M \wedge N = 90° 05'$, $L \wedge N = 90° 21'$. The angle between the plane of the molecule and the (010) plane, ψ_N, is 47·0°. For coronene[3] the corresponding angle is 43·7°.

Standard deviations. The standard deviations of the atomic positions were calculated from Cruickshank's [4] formulæ. The mean values for all the atoms are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}020$ Å, so that the standard deviations of the individual bond distances are 0·028 Å. This value may be compared with the root-mean-square deviation of the individual bond lengths from the mean

[4] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

values, 0·032 Å. The standard deviations of the mean bond distances are $0{\cdot}028/\sqrt{3} = 0{\cdot}016$ Å where three independent estimates are available, and $0{\cdot}028/\sqrt{6} = 0{\cdot}011$ Å where six independent measurements have been made. These accuracy calculations reflect the measure of agreement that we have been able to obtain with the available data. As the amount of these data is small, owing to poor-quality crystals, the actual errors in the bond length estimates may be greater than is indicated by these standard calculations.

Intermolecular distances. All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation *b* is 3·48 Å, but the individual atoms are not vertically over each other. Indeed there is a pronounced tendency to avoid such overlap, as can be seen from Fig. 3, which shows the normal projection of two parallel molecules separated by translation *b*. The corresponding perpendicular distance in coronene is 3·40 Å. The shorter lateral contacts are illustrated in Fig. 4.

TABLE 3. *Measured and calculated structure factors.*

h k l	$\lvert F_o\rvert$	F_c	*h k l*	$\lvert F_o\rvert$	F_c	*h k l*	$\lvert F_o\rvert$	F_c	*h k l*	$\lvert F_o\rvert$	F_c	*h k l*	$\lvert F_o\rvert$	F_c	*h k l*	$\lvert F_o\rvert$	F_c
0 0 1	85·0	+91·5	1	19·0	+19·2	0	28·8	−23·8	$\bar{4}$	21·9	+23·3	$\bar{6}$	24·0	+22·5	1	28·7	−27·4
2	60·6	−61·1	2	15·0	−14·9	1	69·0	−60·4				$\bar{4}$	8·2	+7·9	2	34·8	−38·8
3	3·7	−4·4	3	6·2	−10·5	2	5·6	−4·5	0 1	1	5·1	+3·2	$\bar{2}$	20·2	+26·7	3	11·6	+8·0
4	18·3	+20·2	4	6·2	+8·7	5	5·6	−12·9		2	8·1	−8·5	1	170·9	−171·0	7	33·4	+30·8
5	61·5	−60·1	5	6·0	−4·1	6	45·7	+47·9		3	8·0	−9·5	0	75·3	−77·7	8 1 $\bar{10}$	41·3	+42·2
6	58·7	−60·3	8	8·9	+9·4	7	32·5	+35·0		5	5·9	−4·0	1	25·4	+30·4	$\bar{5}$	10·9	+9·2
7	10·5	+10·9	6 0 $\bar{10}$	7·6	+8·1	8	5·3	−5·0		8	8·1	+14·4	5	31·6	+35·0	$\bar{5}$	21·3	−16·5
11	11·9	−11·3	7	7·0	−6·1	12 0 $\bar{11}$	45·7	+55·3	1 1	$\bar{5}$	18·6	+19·2	7	9·7	+2·8	$\bar{4}$	48·9	−51·0
2 0 $\bar{12}$	15·3	−23·8	$\bar{4}$	16·7	−18·4	$\bar{10}$	24·4	+26·4		$\bar{4}$	8·1	−15·9	8	17·7	+13·7	$\bar{3}$	8·5	+11·7
$\bar{11}$	12·3	−19·7	$\bar{3}$	5·1	−2·4	$\bar{9}$	7·8	−10·0		$\bar{2}$	22·2	+21·3	5 1 $\bar{7}$	25·6	−23·0	$\bar{2}$	9·8	+13·9
$\bar{8}$	10·8	+10·4	$\bar{2}$	12·5	+9·7	$\bar{7}$	9·4	+8·0		$\bar{1}$	33·8	−41·2	$\bar{6}$	29·4	−34·6	$\bar{1}$	14·0	+16·5
$\bar{7}$	11·5	−14·6	$\bar{1}$	49·0	+46·5	$\bar{6}$	28·8	−19·9		0	Not	+7·9	$\bar{3}$	9·6	−8·3	1	29·7	−29·2
$\bar{6}$	77·3	−75·7	2	5·1	+3·8	$\bar{5}$	62·7	−54·4			observed		$\bar{1}$	101·0	+91·3	9 1 $\bar{10}$	32·9	+35·6
$\bar{5}$	6·1	−3·7	3	6·9	+10·1	$\bar{4}$	2·7	−0·6		1	36·0	−33·7	0	12·2	+7·0	$\bar{6}$	8·3	+6·9
$\bar{3}$	26·1	+26·3	4	14·2	−20·6	$\bar{3}$	3·9	+5·3		2	25·2	+27·5	1	8·3	−6·8	$\bar{5}$	28·7	−31·7
$\bar{2}$	33·0	−34·4	5	6·7	+10·3	$\bar{1}$	7·5	+8·8		3	14·5	−15·2	2	25·0	−24·9	$\bar{4}$	10·8	−9·7
$\bar{1}$	70·5	+76·5	6	8·4	−10·4	0	36·4	−28·1		4	10·7	+13·1	5	8·6	−2·0	1	14·3	−13·0
0	86·0	+93·3	7	6·3	−5·0	1	20·9	−18·2		5	18·0	−20·2	7	22·5	+24·1	10 1 $\bar{10}$	12·8	+11·4
1	42·5	−40·0	8	9·2	−10·0	6	11·0	+9·3		$\bar{6}$	7·9	−8·8	8	23·5	+18·1	$\bar{2}$	21·3	−21·5
2	57·7	+50·3	8 0 $\bar{9}$	8·4	−11·7	7	5·1	−4·6	2 1	$\bar{3}$	27·6	−25·9	6 1 $\bar{7}$	29·6	+29·6	13 1 0	16·0	−13·1
3	18·3	−19·1	$\bar{8}$	6·8	+7·4	14 0 $\bar{13}$	9·9	+9·5		0	26·0	−40·0	$\bar{4}$	35·0	−34·8	14 1 0	19·6	+16·7
4	17·9	+16·4	$\bar{7}$	8·2	−13·9	$\bar{11}$	23·5	+25·7		1	12·8	+14·1	$\bar{1}$	30·2	−33·1	15 1 $\bar{12}$	8·4	+8·6
6	11·0	+11·9	$\bar{5}$	14·3	+17·6	$\bar{3}$	10·2	−8·8		2	11·9	−8·3	0	21·8	+23·0	$\bar{11}$	14·5	+14·3
7	3·9	−1·8	$\bar{4}$	13·6	+13·9	$\bar{2}$	3·1	−4·9		3	6·9	+3·1	1	45·8	−43·5	$\bar{6}$	21·0	−17·9
$\bar{8}$	5·9	−4·4	$\bar{2}$	16·6	−15·6	$\bar{1}$	3·1	+5·7		5	25·4	+22·4	2	35·0	−31·2	0	16·9	−15·3
4 0 $\bar{12}$	8·1	−8·0	$\bar{1}$	16·8	−20·8	0	3·2	+4·3		6	16·4	+19·2	5	7·8	−9·9	16 1 $\bar{12}$	14·5	−14·7
$\bar{9}$	13·0	−14·5	0	7·5	+6·4	1	10·3	+8·1		7	12·8	−12·0	7	41·4	+38·3	$\bar{11}$	12·2	−14·0
$\bar{7}$	9·0	+5·1	2	7·7	+6·9	16 0 $\bar{11}$	7·6	−6·7	3 1	$\bar{6}$	24·0	−30·1	$\bar{8}$	15·1	+15·9	$\bar{6}$	15·8	+17·9
$\bar{6}$	12·3	+11·7	7	26·2	+29·5	$\bar{3}$	6·5	+9·7		$\bar{2}$	17·8	−19·0	7 1 $\bar{10}$	17·8	+14·1	17 1 $\bar{12}$	13·6	+13·5
$\bar{5}$	12·3	+7·8	12	5·9	−5·8	18 0 $\bar{3}$	7·9	−5·5		$\bar{1}$	110·8	+135·3	$\bar{8}$	6·3	−5·0	18 1 $\bar{12}$	9·0	−8·3
$\bar{4}$	27·2	−26·3	10 0 $\bar{5}$	39·3	−38·8	20 0 $\bar{4}$	10·0	+8·6		0	101·4	+102·2	$\bar{7}$	7·2	−7·1	$\bar{4}$	25·6	+20·6
$\bar{3}$	53·6	+54·4	$\bar{4}$	17·0	−12·6	1	6·9	−3·3		1	15·5	−18·0	$\bar{6}$	7·8	+8·5	$\bar{3}$	18·0	+17·2
$\bar{2}$	39·5	−46·1	$\bar{3}$	7·6	+6·6	2	9·9	−6·3		3	16·8	+19·9	$\bar{5}$	20·3	−21·1	19 1 $\bar{4}$	20·4	+19·3
$\bar{1}$	34·0	−35·6	$\bar{2}$	3·4	−5·6	22 0 $\bar{10}$	10·5	−8·9		5	39·4	−39·3	$\bar{4}$	37·1	−30·5			
0	48·1	−54·4	$\bar{1}$	13·1	+10·6	$\bar{5}$	17·5	+16·2	4 1	7	22·8	+23·6	$\bar{1}$	9·0	−7·2			

Discussion.—The carbon skeleton of hexabenzocoronene is probably planar within the limits of experimental error, the maximum deviation of the atoms from the mean plane being 0·065 Å, and the root-mean-square deviation 0·024 Å. The indications for the "overcrowded" positions (1 and 5, 3 and 11, 13 and 21) are very similar to those for 1,2:7,8-dibenzocoronene.[1]

The mean bond distances show little variation over the molecule. The bonds radiating from the central ring are the longest in the molecule, but none of the differences is really significant. Better crystals would be required to define the bond distances with greater precision.

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249. *Steric Effects in Di- and Tri-arylmethanes. Part III.* Electronic Absorption Spectra of Derivatives of Malachite Green containing Substituents in the Phenyl Ring.*

By C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp.

Absorption spectra of derivatives of Malachite Green containing substituents in the phenyl ring have been examined. With the exception of the nitro-group, substituents in the 3- or 4-position have little effect on the maximum intensity of the first frequency band but they modify the position of the band to an extent which is linearly related to the appropriate Hammett substituent constant. Substituents in the 2-position, however, markedly increase the intensity of this band, and this increase varies directly with the van der Waals radius of the substituent except in the case of the t-butyl group. Substituents in the 2-position also bring about a bathochromic shift of the first band relative to that of the 4-substituted isomer.

An equilibrium between the methyl ether of the 2-hydroxy-derivative of Malachite Green base and the zwitterion (VII) in methanol is described.

Introduction of a substituent at the central carbon atom of a diphenylmethane dye brings about spectral changes caused by the donation or withdrawal of electrons and by a change in the molecular conformation. The central carbon atom is at an " inactive " position,[1] that is, one with unit π-electron density,[2] and molecular-orbital theory predicts [3] that substituents with $-E$ (electron-donating) activity should produce hypsochromic shifts whereas $+E$ or $\pm E$ substituents should produce bathochromic shifts. The crowding effect of substituents at the central carbon atom should also result in bathochromic shifts.[4] The purely electronic effect can be demonstrated by introducing a small group with a large $-E$ effect. Thus, Michler's Hydrol Blue (I; R = H; $\lambda_{max.}$ 607·5 mμ) absorbs at much longer wavelength than its α-amino-derivative Auramine (I; R = NH_2; $\lambda_{max.}$ 435 mμ), but a more versatile approach is to compare the positions of the first frequency band of derivatives of Malachite Green (II) containing substituents in the 3- and 4-position. Malachite Green shows two absorption bands in the visible region (Fig. 1), the major band corresponding to polarisation along the x-axis of the molecule,[5] the minor band corresponding to polarisation along the y-axis.

Contrary to a statement by Dewar,[3] the carbon atoms of the phenyl ring in Malachite Green cannot be divided into " active " and " inactive," the π-electron density being uniform,[2] so that alternation of electronic effect round the phenyl ring is not observed and it is found [6] that the spectral shifts brought about by substituents in the 3- or 4-position are directly proportional to the appropriate Hammett substituent constant,[7] the strongly conjugated 4-hydroxy- and 4-methoxy-group being excepted (Fig. 2). The effect of the last two groups is described better by the use of the electrophilic substituent constants evaluated by Brown.[8] The simplicity of this relation depends upon the fact that the first frequency band originates in a transition from the non-bonding molecular orbital to the first unoccupied molecular orbital and it is the energy of the latter orbital only which is changed by substituents, whereas the second frequency band originates

* Part II, *J.*, 1960, 3790.

[1] Dewar, " Recent Advances in the Chemistry of Colouring Matters," *Chem. Soc. Special Publ.*, No. 4, 1956, p. 79.
[2] Itoh, *J. Phys. Soc. Japan*, 1957, **12**, 644.
[3] Dewar, *J.*, 1950, 2329.
[4] Barker, Bride, and Stamp, *J.*, 1959, 3957.
[5] Bigeleisen and Lewis, *J. Amer. Chem. Soc.*, 1943, **65**, 2102.
[6] Barker, " Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths, London, 1958, p. 38.
[7] Jaffé, *Chem. Rev.*, 1953, **53**, 222.
[8] Brown, " Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths, London, p. 109.

in a transition from the highest occupied bonding orbital to the first unoccupied orbital, and the energies of both of these orbitals are changed by substituents.

Substitution in the 2-position of Malachite Green produces a unique spectral response which is clearly illustrated by the effect of introducing the methyl group. Whereas 3- amd 4-methyl groups produce small hypsochromic shifts of the *x*-band and leave $\varepsilon_{max.\ (x)}$

TABLE 1. *Absorption max.* (mμ) ($10^{-4}\varepsilon$ *in parentheses*) *for derivatives of Malachite Green in* 98% *acetic acid.*

Subst.				Subst.			
None	621	(10·4);	427·5 (2·0)	4-Br	628	(10·4);	435 (2·3)
2-Me	622·5	(12·3);	420 (1·5)	2-I	635	(12·8);	417·5 (1·3)
3-Me	618·5	(10·6);	433 (2·2)	3-I	630·5	(10·3);	429 (1·9)
4-Me	616·5	(10·6);	437·5 (2·5)	4-I	628	(10·3);	437·5 (2·5)
2,6-Me_2	624	(13·2);	410 (1·2)	2-MeO	625	(11·5);	442 (1·3)
2-Bu^t	623·5	(11·8);	415 (1·4)	3-MeO	622·5	(10·7);	435 (1·8)
4-Bu^t	616	(10·4);	440 (2·6)	4-MeO	608	(10·6);	465 (3·4)
2-F	635	(11·3);	424 (1·6)	4-MeO-2-Me	614	(12·4);	460 (2·2)
3-F	630	(10·4);	426·5 (2·2)	2-OH	621	(11·4);	447·5 (1·3)
4-F	620	(10·6);	430·5 (2·1)	4-OH	602·5	(10·6);	470 (3·6)
2-Cl	635	(12·1);	415·5 (1·3)	4-OH-2-Me	610	(12·1);	465 (2·4)
3-Cl	630	(10·3);	426 (1·7)	2-NO_2	637·5	(9·8);	415 (1·2)
4-Cl	627·5	(10·4);	433 (2·2)	3-NO_2	637·5	(8·7);	425 (1·4)
2-Br	636	(12·3);	415 (1·3)	4-NO_2	645	(8·3);	425 (1·7)
3-Br	630	(10·4);	427·5 (1·8)				

FIG. 1. *Absorption spectra of* (1) *methyl* 4′,4″-*bisdimethylamino*-2-*hydroxytriphenylmethyl ether in methanol* [$10^{-2}\varepsilon$ *plotted*], *and* (2) *Malachite Green in* 98% *acetic acid. (Reproduced, with permission, from "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London,* 1959, p. 37.)

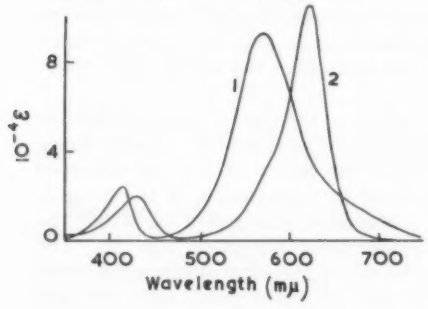
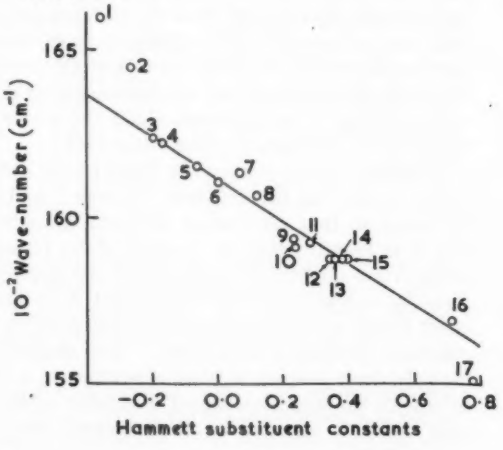


FIG. 2. *Relation between σ-constants and* $\lambda_{max.\ (x)}$ *of derivatives of Malachite Green.* 1, 4-OH; 2, 4-OMe; 3, 4-t-Bu; 4, 4-Me; 5, 3-Me; 6, unsubstituted; 7, 4-F; 8, 3-OMe; 9, 4-Cl; 10, 4-Br; 11, 4-I; 12, 3-F; 13, 3-I; 14, 3-Cl; 15, 3-Br; 16, 3-NO_2; 17, 4-NO_2. (*Reproduced, with permission, from "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London,* 1959, *p.* 38.)



essentially unchanged (106,000 compared with 104,000 for the parent dye), the 2-methyl group produces a small bathochromic shift and a marked increase in $\varepsilon_{max.\ (x)}$ (123,000; Table 1). This increase is exaggerated in the 2,6-dimethyl derivative ($\varepsilon_{max.\ (x)}$ 132,000). The 2-methyl group must produce a crowding effect and the bathochromic shift is consistent with rotation of the dimethylaminophenyl groups about the central bond, but this shift should be accompanied by a decrease in the value of $\varepsilon_{max.\ (x)}$ instead of the observed increase. The *y*-band responds to the introduction of the 2-methyl group by a hypsochromic shift and a marked reduction in intensity (Table 1), effects which are

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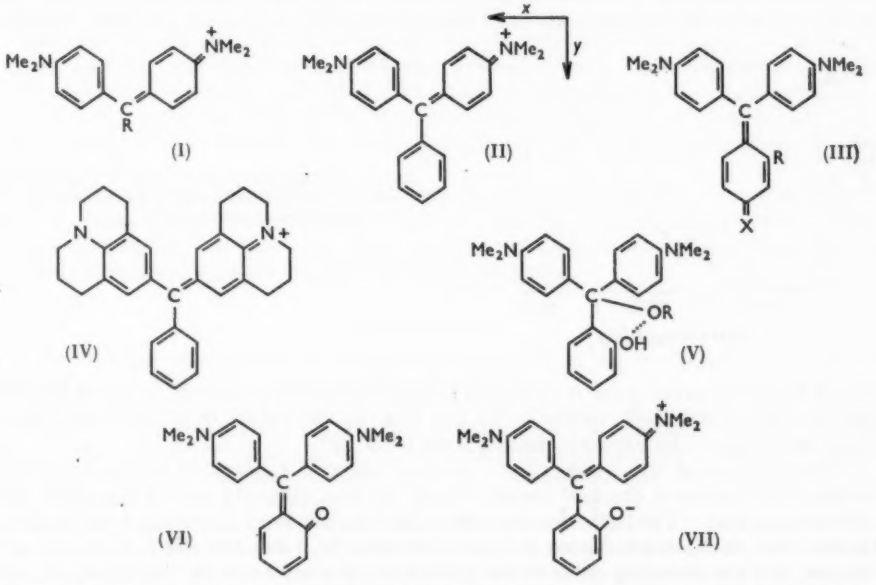
consistent with increased departure from molecular uniplanarity along the *y*-axis of the molecule and can be attributed to rotation of the dimethylaminophenyl or phenyl group about the central bonds. An alkyl group in the 3- or 4-position produces a bathochromic shift and increases the intensity of the *y*-band.

The spectra of the halogeno-derivatives of Malachite Green show the same general pattern as the spectra of the methyl derivatives (Table 1). The 3- and 4-halogeno-compounds give values of $\varepsilon_{max.\ (x)}$ in the range 103,000—106,000, whereas the 2-halogeno-derivatives give values (113,000—128,000) which vary directly with the van der Waals radii of the halogen atoms. Also, the *x*-bands of the 2-halogeno-derivatives occur at slightly longer wavelength than those of the 3-halogeno-isomers and these absorb at longer wavelength than the *x*-band of the parent dye owing to electron-withdrawal by the halogen. This bathochromic effect of the halogen is reduced in the 4-halogeno-compounds by mesomeric interaction with the central carbon atom (III; R = H, X = Cl^+). This mesomerism also results in increased intensity of the *y*-band (Table 1).



The 2-methoxy- and the 2-hydroxy-derivative also show increased values of $\varepsilon_{max.\ (x)}$ (115,000 and 114,000, respectively), values which suggest that it is the radius (1·40 Å) of the oxygen atom alone which governs the absorption intensity, a view consistent with the value of 113,000 for $\varepsilon_{max.\ (x)}$ observed when the 2-fluoro-group (radius 1·35 Å) is present. The *x*-bands of the methoxy- and hydroxy-compound do not, however, show pronounced bathochromic shifts when compared with the *x*-band of the parent dye, but they do so when compared with the corresponding 4-substituted isomer in which mesomerism involving the terminal oxygen atom (III; R = H, X = $^+$OH or $^+$OMe) reduces $\lambda_{max.\ (x)}$ and increases $\varepsilon_{max.\ (y)}$.

The correspondence between effective radius of a substituent in the 2-position and the value of $\varepsilon_{max.\ (x)}$ is inconsistent with the low value (118,000) observed with the 2-t-butyl derivative of Malachite Green, but it is probable that the exceptionally large t-butyl group produces exceptional conformational changes.

The 2-nitro-derivative of Malachite Green also shows an " *ortho*-effect," but the normal bathochromic shift is obscured by a reduction in the $+E$ activity of the nitro-group

caused by partial rotation of this group about the bond joining it to the phenyl ring. Also, all the nitro-derivatives give *x*-bands of rather low intensity, a phenomenon which may be associated with the $+E$ activity of the nitro-group.

The crowding effect of *ortho*-groups in derivatives of triphenylmethanol decreases their stability relative to that of the corresponding carbonium ions. Thus, Deno *et al.*[9] obtained pK_b values of $-1{\cdot}96$ and $-2{\cdot}47$ for *o*- and *p*-tritolylmethanol, respectively, so that the increased values of $\varepsilon_{max.\ (x)}$ observed with the 2-substituted derivatives of Malachite Green could be caused by displacement of the dye base–dye equilibrium. Interpreted in this way, the values of $\varepsilon_{max.\ (x)}$ of 104,000 and 132,000 obtained with Malachite Green and its 2,6-dimethyl derivative, respectively, imply that in 98% acetic acid the parent dye is ionised only to the extent of 79%. If ionisation is so incomplete, the constancy of the values of $\varepsilon_{max.\ (x)}$ obtained with the 3- and 4-substituted derivatives is surprising. The substituents would be expected to modify the position of the dye base–dye equilibrium, and the failure of the strongly conjugated 4-methoxy- and 4-hydroxy-group to do so is particularly significant. Further strong evidence for the view that these dyes are completely ionised in 98% acetic acid comes from the observation that the julolidine analogue

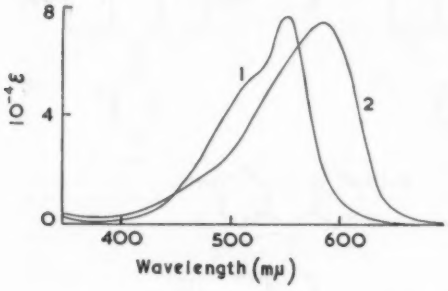


FIG. 3. *Absorption spectra of* (1) *4′,4″-bisdimethylaminofuchsone,* (2) *4′,4″-bisdimethylamino-2-methylfuchsone in methanol.*

(IV) of Malachite Green, to be described in a later paper, gives a value of $\varepsilon_{max.\ (x)}$ of 109,000, and this dye is stabilised relative to its dye base by the release of strain which occurs when the nitrogen hybridisation changes from sp^3 to sp^2.

Interpretation of the "*ortho*-effect" is made difficult by lack of knowledge of the precise conformational changes brought about by 2-substituents and of the exact rôle of the phenyl ring. The bathochromic shift of 13·5 mμ observed on passing from Michler's Hydrol Blue to Malachite Green is consistent with the predicted effect of a $\pm E$ substituent, but the crowding effect of the phenyl group should also be bathochromic, and until the relative magnitude of these spectral shifts is known it is difficult to assess the effect of rotating the phenyl ring in Malachite Green. A comparable study of bridged compounds of known conformation may shed light on the problem.

The colourless methyl ether of the 2-hydroxy-derivative of Malachite Green base (V; R = Me) is unusual in that it dissolves in methanol to give a blue solution with the spectrum shown in Fig. 1. It is probable that in methanol an equilibrium exists between the methyl ether and the merocyanine (VI) formed by elimination of methanol, but the spectrum ($\lambda_{max.}$ 570, 415 mμ; ε 925, 240), although weak is very similar to that of Malachite Green and quite different from that (Fig. 3) of 4′,4″-bisdimethylaminofuchsone (III; R = H, X = O), observations which suggest that the highly polarised form (VII) makes the major contribution to the resonance hybrid. This high degree of polarisation is probably caused by the high energy of the *ortho*-quinonoid structure rather than by a steric effect because the hindered fuchsone (III; R = Me, X = O) gives a spectrum (Fig. 3) which is similar to that of the unhindered compound (III; R = H, X = O).

[9] Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 159.

It may be recalled that the 4-hydroxy-derivative of Malachite Green gives 4',4''-bis-dimethylaminofuchsone when basified.

The ether (V; R = Me) separates from methanolic sodium methoxide as the free phenol, a fact most readily explained by intramolecular hydrogen bonding, but the OH stretching frequency, measured in a " Nujol " mull or potassium bromide pellet, is 3300 cm.$^{-1}$ which implies polymeric association, whereas dilution of a carbon tetrachloride solution from 5% to 0·1% changed the frequency only from 3320 to 3340 cm.$^{-1}$. The free dye base (V; R = H), which was not obtained analytically pure, was precipitated from an aqueous solution of the dye by means of sodium hydroxide. Methanolic solutions of the dye base and its methyl ether gave identical electronic absorption spectra.

Preparations.—The majority of the dyes was prepared by condensing the appropriate aldehyde with *NN*-dimethylaniline in acid solution and oxidising the resultant leuco-compound with lead dioxide in the presence of hydrochloric acid. The dyes were ultimately isolated as the readily purified methyl ethers of the dye bases. The preparation of the 3-nitro-derivative of Malachite Green, described in the Experimental section, represents a typical case.

The method of Rodd and Linch,[10] which uses the interaction of a mixture of Michler's ketone, sodium, and aryl halide in toluene, succeeded with 4-iodo-t-butylbenzene and 2-chloro-5-methoxytoluene but failed with 2-iodo-t-butylbenzene and 2-iodo-*m*-xylene, but by first converting these halides into the corresponding lithium compounds, interaction with Michler's ketone was achieved smoothly. Both of these processes yielded the dye base.

The 4-hydroxy- and the 4-hydroxy-2-methyl derivative of Malachite Green were isolated as the corresponding fuchsones (III; X = O, R = H and Me, respectively). These fuchsones, and the dye bases and their methyl ethers, regenerated the original dyes in the 98% acetic acid used for the spectral determinations.

Experimental

The following preparations are quoted as illustrations of the methods A, B, C, and D referred to in Table 3. For details see Tables 2 and 3.

Method A. Methyl 4,4'-Bisdimethylamino-3''-nitrotriphenylmethyl Ether.—*m*-Nitrobenzaldehyde (15·5 g.), ethanol (75 c.c.), *NN*-dimethylaniline (36·8 g.), and 36% hydrochloric acid (24·0 g.) were mixed and refluxed for 24 hr. The mixture was basified with aqueous ammonia, the excess of *NN*-dimethylaniline was removed by steam-distillation, and the residual base was crystallised from 1 : 1 benzene–ethanol.

This base (3·75 g.) was dissolved in water (60 c.c.) and 36% hydrochloric acid (4·0 g.). The stirred solution was cooled to 0° by addition of crushed ice, and an aqueous paste of lead dioxide, prepared [11] from lead nitrate (3·30 g.), was added in one portion. The resultant suspension was warmed to 60°, hydrated sodium sulphate (5·0 g.) was added, and the lead sulphate was removed. Hydrated sodium acetate (1·36 g.) followed by sodium chloride (15 g.) were then added, whereupon the dye separated as a tar which became crystalline overnight and was washed with aqueous sodium chloride (15%) and dried at 60°.

A solution of this dye (2·7 g.) in methanol (20 c.c.) was slowly added to methanol (40 c.c.) containing sodium methoxide (0·9 g.). The resultant *ether* separated as yellow crystals which were washed with methanol and crystallised from 3 : 1 methanol–benzene.

Method B. Methyl 4-Chloro-4',4''-bisdimethylaminotriphenylmethyl Ether.—A warm solution of Michler's ketone (13·4 g.) in dry pyridine (70 c.c.) was added to the Grignard reagent from *p*-chloroiodobenzene (19·2 g.) and magnesium (2·4 g.) in ether (100 c.c.). After 20 min. the mixture was poured into aqueous ammonium chloride and 24 hr. later Michler's ketone was filtered off. The ether was removed, the residual dye base was dissolved in N-acetic acid, and the dye oxalate was precipitated by means of oxalic acid and ammonium oxalate. The dried oxalate was converted into the *ether* of the dye base as in method A.

[10] Rodd and Linch, *J.*, 1927, 2174.

[11] Fierz-David and Blangey, " Fundamental Processes of Dye Chemistry," 1949, Interscience Publ. Ltd., London, p. 138.

Method C. **2,6-*Dimethyl*-4′,4″-*bisdimethylaminotriphenylmethanol*.**—The lithium compound from 2-iodo-*m*-xylene (4·64 g.) in ether (20 c.c.) was added to a suspension of Michler's ketone

TABLE 2. *Derivatives of the leuco-base of Malachite Green.*

		Found (%)					Required (%)			
Subst.	M. p.	C	H	N	Hal	Formula	C	H	N	Hal
2-F	131—131·5°	78·9	7·1	8·3		$C_{23}H_{23}FN_2$	79·3	7·2	8·0	
3-F	100·5—101	79·1	7·2	8·4		,,	79·3	7·2	8·0	
4-F	104—104·5	79·5	7·2	7·8		,,	79·3	7·2	8·0	
2-Br	150	67·7	6·5	6·9	18·9	$C_{23}H_{23}BrN_2$	67·5	6·2	6·8	19·5
3-Br	116	67·8	6·2	6·7	18·6	,,	67·5	6·2	6·8	19·5
4-Br	120—120·5°	67·4	6·2			,,	67·5	6·2	6·8	19·5
2-I	142·5—143	61·0	5·5	6·3	27·1	$C_{23}H_{23}IN_2$	60·5	5·5	6·1	27·8
3-I	147—147·5	60·3	5·7	6·2	28·2	,,	60·5	5·5	6·1	27·8
4-I	138·5—139	60·3	5·8	6·3	27·7	,,	60·5	5·5	6·1	27·8
4-OH-2-Me	184—185	79·7	7·8	7·8		$C_{24}H_{28}N_2O$	80·0	7·8	7·8	

° Dutt (*J.*, 1926, 1179) gives m. p. 128°.

TABLE 3. *Derivatives of Malachite Green (as base, methyl ether of the base, or fuchsone).*

			Found (%)					Required (%)			
Subst.	Method °	M. p.	C	H	N	Hal	Formula	C	H	N	Hal
Ethers											
2-F	A	156·5—157°	75·8	7·1	7·3		$C_{24}H_{27}N_2OF$	76·1	7·2	7·4	
3-F	A	149·5—150	76·4	7·3	7·1		,,	76·1	7·2	7·4	
4-F	A	136—136·5	76·2	7·3	7·1		,,	76·1	7·2	7·4	
2-Cl	A	143—143·5	73·1	6·8	7·2	9·2	$C_{24}H_{27}N_2OCl$	73·0	7·8	7·1	9·0
3-Cl	A	135—135·5	72·7	6·7	6·8	8·7	,,	73·0	6·8	7·1	9·0
4-Cl	B	135—136	73·0	6·6	7·2	8·8	,,	73·0	6·8	7·1	9·0
2-Br	A	132	65·8	6·2	6·1	17·8	$C_{24}H_{27}N_2OBr$	65·6	6·2	6·4	18·2
3-Br	A	124—124·5	65·6	6·3	6·1	18·0	,,	65·6	6·2	6·4	18·2
4-Br	A	128—129	65·8	6·3	6·1	17·8	,,	65·6	6·2	6·4	18·2
2-I	A	145·5—146	59·2	5·9	5·7	26·3	$C_{24}H_{27}N_2OI$	59·2	5·6	5·8	26·1
3-I	A	111·5—112	58·8	5·4	5·6	25·7	,,	59·2	5·6	5·8	26·1
4-I	A	135·5—136	59·0	5·7	5·9	27·2	,,	59·2	5·6	5·8	26·1
2-OH	A	138—140	76·6	7·5	7·2		$C_{24}H_{28}N_2O_2$	76·6	7·5	7·4	
2-OMe	B	104—106	76·9	7·9	7·2		$C_{25}H_{30}N_2O_2$	76·9	7·7	7·2	
3-OMe	A	92—93	76·6	7·8	7·0		,,	76·9	7·7	7·2	
4-OMe	B	104—104·5	76·7	7·6	7·1		,,	76·9	7·7	7·2	
2-NO_2	A	138—140	69·7	6·6	10·4		$C_{24}H_{27}N_3O_3$	71·1	6·7	10·4	
3-NO_2	A	122—123	71·3	6·7	10·4		,,	71·1	6·7	10·4	
4-NO_2	A	156—157	70·9	6·7	10·4		,,	71·1	6·7	10·4	
Bases											
4-OMe-2-Me	D	97—98	76·8	7·6	7·3		$C_{25}H_{30}N_2O_2$	76·9	7·8	7·2	
2-Me	A	139—140	79·4	7·8	7·7		$C_{24}H_{28}N_2O$	80·0	7·8	7·8	
3-Me	A	136—137	79·5	7·8	7·8		,,	80·0	7·8	7·8	
4-Me	A	159—160	79·8	7·8	7·9		,,	80·0	7·8	7·8	
2,6-Me_2	C	128—129	80·4	8·2	7·6		$C_{25}H_{30}N_2O$	80·2	8·1	7·5	
2-Bu^t	C	160—161	80·5	8·4	6·9		$C_{27}H_{34}N_2O$	80·6	8·5	7·0	
4-Bu^t	D	164—166	80·2	8·3	7·2		,,	80·6	8·5	7·0	
Fuchsones											
4-OH	A	Decomp.	80·0	6·9	8·0		$C_2H_{24}N_2O$	80·2	7·0	8·1	
4-OH-2-Me	A	*ca.* 210	80·1	7·2	7·8		$C_{21}H_{26}N_2O$	80·4	7·3	7·8	

(1·34 g.) in ether (50 c.c.). Water (250 c.c.) was added to the mixture after 1 hr. Removal of ether from the dried (Na_2SO_4) organic layer gave the base as a blue gum which crystallised from 75% ethanol.

Method D. **4,4′-*Bisdimethylamino*-4″-*t-butyltriphenylmethanol*.**—Sodium (4·6 g.), Michler's ketone (26·8 g.) and *p*-iodo-t-butylbenzene (18 c.c.) were refluxed in an atmosphere of nitrogen for 24 hr. Water (250 c.c.) was added to the reaction mixture and the dye base was isolated from the dried (Na_2SO_4) benzene layer and crystallised four times from ethanol containing a trace of sodium hydroxide.

The authors acknowledge grants from the Department of Scientific and Industrial Research (to G. H.) and the Hull Education Authority (to M. H. B. and A. S.), and thank Dr. G. W. Gray for infrared spectral determinations.

THE UNIVERSITY, HULL.

[*Received, September 12th*, 1960.]

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250. *Di-N-substituted 2-Halogenoethylamines. Part V.*[1] *Fluorenylamine, Thenylamine, and Thionaphthenylmethylamine Derivatives: their Synthesis, Reactivity, and Pharmacology.*

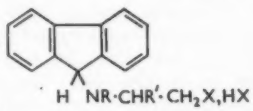
By N. B. Chapman and A. J. Tompsett.

The synthesis of a series of *N*-ethyl-*N*-2′-halogenoethyl-, *N*-ethyl-*N*-2′-halogenopropyl-, and *N*-benzyl-*N*-2′-halogenoethyl-9-fluorenylamines; of some *N*-ethyl-*N*-2′-halogenoethyl-3-thionaphthenylmethylamines; and of some *N*-benzyl-*N*-2′-halogenoethyl-2-thenylamines is described. The decomposition undergone by some of these compounds in aqueous acetone at various temperatures is shown graphically. The anti-adrenaline and anti-noradrenaline activity of two of the fluorenylamine derivatives, which are of extraordinary potency, are strongly correlated with ethyleniminium ion concentration by the method used in Parts II and III, and the pharmacological properties of all the compounds prepared are briefly reported (cf. Graham, ref. 15). Piperazinium salts, probably formed in the decomposition of the compounds, are shown to be inactive against adrenaline and noradrenaline.

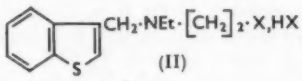
The influence of isosteric replacement on the relation between chemical structure and reactivity, and on pharmacological activity is briefly discussed in relation to the properties of the thenylamine and thionaphthenylmethylamine compounds prepared.

Finally the discrepancies in previous reports of the decomposition of dibenamine [$N(CH_2Ph)_2 \cdot CH_2 \cdot CH_2Cl,HCl$] in aqueous solvents have been resolved.

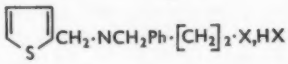
The object of the present paper is to broaden our study of the relation between structure, reactivity, and pharmacological activity in this field by including compounds of the types (I—III) with X = Cl, Br, or I, and R = Et, R′ = H or Me, and R = CH_2Ph, R′ = H. Moreover, as all our previous reactivity studies had been carried out at a temperature of 30°, different from that pertaining *in vivo*, in certain cases reactivity at 19°, 37°, and 45°



(I)



(II)



(III)

was studied. Although some of the 9-fluorenylamine derivatives have been previously reported by Kerwin, Herdegen, Heisler, and Ullyot [2] and by Rieveschl,[3] and their pharmacological properties studied by Stone, Komrad, and Loew,[4] most of them are new and have not been investigated pharmacologically. Improvements in existing synthetic processes have also been made and intermediates thoroughly characterised. *N*-2′-Chloroethyl-*N*-ethyl-3-thionaphthenylmethylamine hydrochloride has previously been reported in a patent by Avakian and Martin,[5] but because of the close similarity of compounds of this type to the 1-naphthylmethyl derivatives studied by Chapman and James,[6] it was felt that they were worthy of further investigation. The interest of the thenylamine derivatives lies in their similarity to dibenamine [$N(CH_2Ph)_2 \cdot CH_2 \cdot CH_2Cl,HCl$], the

[1] Part IV, Chapman and Allen, *J.*, 1961, 1076.
[2] Kerwin, Herdegen, Heisler, and Ullyot, *J. Amer. Chem. Soc.*, 1950, **72**, 940.
[3] Rieveschl, U.S.P. 2,573,607—8; cf. *Chem. Abs.*, 1952, **46**, 9607.
[4] Stone, Komrad, and Loew, *Arch. Internat. Pharm.*, 1952, **92**, 7.
[5] Avakian and Martin, U.S.P. 2,553,495; cf. *Chem. Abs.*, 1952, **46**, 537.
[6] Chapman and James, *J.*, 1954, 2103.

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behaviour of which in aqueous solvents has been re-investigated in order to resolve the contradictions in the reports of previous workers.[6,7]

Interaction of 9-bromofluorene with *N*-ethyl-2-hydroxyethylamine, *N*-ethyl-2-hydroxypropylamine, or *N*-benzyl-2-hydroxyethylamine gave *NN*-disubstituted hydroxy-amines from which the corresponding halogeno-compounds were prepared by the method of Chapman and James.[6] 3-Thionaphthenylmethyl and 2-thenyl chloride, the essential starting materials in analogous syntheses of compounds of type (II or III), were obtained by chloromethylation of thionaphthen and thiophen respectively.

Experimental

Difficulty was met in analysis of some of these new 2-halogenoalkylamine hydrohalides for nitrogen, and occasionally for iodine because of the unusually high percentages of halogen. In several cases, therefore, carbon, hydrogen, and halogen determinations have been taken as sufficient to identify the compounds and in two cases carbon and hydrogen alone. Picrylsulphonates have been analysed for carbon and hydrogen only.

Preparation of Materials.—*9-Fluorenylamine derivatives.* Bromination of fluorene, m. p. 110—112°, by Wittig and Felletschin's method [8] gave 9-bromofluorene, which on treatment with *N*-ethyl-2-hydroxyethylamine by the method of Kerwin *et al.*[2] afforded *N*-ethyl-*N*-2′-hydroxyethyl-9-fluorenylamine hydrochloride (65%), m. p. 195—197° (from ethanol–ether), (lit.,[2] m. p. 202—204°). The *picrylsulphonate* (from ethanol), m. p. 175—176·5° (Found: C, 50·1; H, 4·0. $C_{23}H_{22}N_4O_{10}S$ requires C, 50·5; H, 4·1%), was obtained from the hydrobromide in aqueous solution by the action of an excess of hot aqueous sodium picrylsulphonate.

Adding a suspension of the powdered hydrochloride of the 9-fluorenylamine derivative (16·2 g., 0·056 mole) in dry chloroform with stirring during 30 min. to an ice-cold suspension of phosphorus pentachloride (12·5 g., 0·06 mole) in dry chloroform, followed by boiling for 3—4 hr. and evaporation to dryness, gave a sticky residue which solidified on trituration with dry ether, to yield *N*-2′-chloroethyl-*N*-ethyl-9-fluorenylamine hydrochloride (83%), m. p. 194·5—195·5° (from ethanol) (lit.,[2] 195—196·5°) (Found: Cl, 23·0. Calc. for $C_{17}H_{18}ClN,HCl$: Cl, 23·0%); Kerwin *et al.*[2] used thionyl chloride instead of phosphorus pentachloride in this preparation. Adding a chloroform solution of the former hydrochloride (14·3 g., 0·05 mole) to a stirred ice-cold mixture of phosphorus tribromide (17·0 g., 0·06 mole) and dry chloroform, followed by heating at the b. p. for 6 hr., removal of chloroform, and crystallisation of the residue from dry ethanol, gave *N*-2′-bromoethyl-*N*-ethyl-9-fluorenylamine hydrobromide (75%), m. p. 197·5—198·5° (Found: C, 51·7; H, 4·8; Br, 40·2; N, 3·9. Calc. for $C_{17}H_{18}BrN,HBr$: C, 51·4; H, 4·8; Br, 40·2; N, 3·6%) [*picrylsulphonate*, m. p. 196—198° (Found: C, 45·3; H, 3·5. $C_{23}H_{21}BrN_4O_9S$ requires C, 45·3; H, 3·6%)]. *N-Ethyl-N-2′-iodoethyl-9-fluorenylamine hydriodide* (72%), m. p. 167—168° (from dry ethanol), was prepared similarly by using phosphorus tri-iodide (Found: C, 41·6; H, 3·7; I, 52·0. $C_{17}H_{18}IN,HI$ requires C, 41·6; H, 3·9; I, 51·7%).

N-Benzyl-*N*-2′-hydroxyethyl-9-fluorenylamine hydrochloride, m. p. 175—178°, was prepared by the method of Kerwin *et al.*[2] using *N*-benzyl-2-hydroxyethylamine, b. p. 118—125°/1 mm., prepared by Rumpf and Quass's method.[9] The base gave a *picrate*, m. p. 157·5—159·5° (from aqueous ethanol) (Found: C, 62·1; H, 4·0; N, 10·7. $C_{28}H_{24}N_4O_8$ requires C, 61·8; H, 4·3; N, 10·3%), and a *picrylsulphonate*, m. p. 194·5—196° (from dry ethanol) (Found: C, 55·0; H, 4·0. $C_{29}H_{24}N_4O_{10}S$ requires C, 55·3; H, 4·0%). *N*-Benzyl-*N*-2′-chloroethyl- [hydrochloride, m. p. 184—186° (lit.,[2] 184—186°)], *N*-benzyl-*N*-2′-bromoethyl- [*hydrobromide*, m. p. 180—182° (from chloroform) (86%) (Found: C, 57·5; H, 4·5; Br, 35·0. $C_{23}H_{20}BrN,HBr$ requires C, 57·6; H, 4·6; Br, 34·8%)], and *N*-benzyl-*N*-2′-iodoethyl-9-fluorenylamine [*hydriodide*, m. p. 172—173·5° (from much dry ethanol) (60%) (Found: C, 47·6; H, 3·8. $C_{23}H_{20}IN,HI$ requires C, 47·8; H, 3·8%)], were prepared from the corresponding alcohols in the usual way.

N-Ethyl-*N*-2′-hydroxypropyl-9-fluorenylamine hydrochloride (72%), m. p. 187·5—189°, was prepared by the method of Kerwin *et al.*[2] using *N*-ethyl-2-hydroxypropylamine (prepared

[7] Harvey and Nickerson, *J. Pharmacol.*, 1953, **109**, 328.
[8] Wittig and Felletschin, *Annalen*, 1944, **555**, 138.
[9] Rumpf and Quass, *Bull. Soc. chim. France*, 1943, **10**, 347.

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by Krasouskii's method [10]), b. p. 69—70°/16 mm., and from it were prepared by the usual methods *N*-2′-chloropropyl- [hydrochloride (64%), m. p. 156·5—157·5° (from ethanol–ether) (cf. Kerwin *et al.*[2])] and *N*-2′-bromopropyl-*N*-ethyl-9-fluorenylamine [*hydrobromide* (78%), m. p. 147·5—148·5° (from ethanol–ether) (Found: C, 52·3; H, 5·6; Br, 38·2. $C_{18}H_{20}BrN,HBr$ requires C, 52·6; H, 5·5; Br, 38·9%)].

3-Thionaphthenylamine Derivatives.—3-Chloromethylthionaphthen, m. p. 37·5—39° [from light petroleum (b. p. 60—80°)], b. p. 100—105°/0·2 mm., was prepared (40% yield) by Avakian and Martin's method [5] (Found: C, 60·3; H, 4·2. Calc. for C_9H_7ClS: C, 59·2; H, 3·9%; suggesting contamination with thionaphthen). Interaction of the chloromethyl compound (37·2 g., 0·2 mole) and *N*-ethyl-2-hydroxyethylamine (37·2 g., 0·42 mole) in benzene at the b. p. for 6 hr., followed by addition of an excess of dry ether, storage at 0° overnight, and removal of *N*-ethyl-2-hydroxyethylamine hydrochloride, gave a filtrate, which on saturation with dry hydrogen chloride at 0° gave *N*-ethyl-*N*-2′-hydroxyethyl-3-thionaphthenylmethylamine hydrochloride, m. p. 127·7—129° (from ethanol–ether) (79%) (lit.,[5] 129—130°), pure enough for further synthetic work [*picrylsulphonate*, m. p. 159—160° (from aqueous acetone) (Found: C, 43·6; H, 4·0. $C_{19}H_{20}N_4O_{10}S_2$ requires C, 43·2; H, 3·8%); *picrate*, m. p. 128—129° (from aqueous ethanol) (Found: C, 49·1; H, 4·2; S, 6·6. $C_{19}H_{20}N_4O_8S$ requires C, 49·1; H, 4·3; S, 6·9%)]. The *N*-2′-hydroxyethyl compound was then converted by the usual methods into *N*-2′-chloroethyl- [hydrochloride (100%), m. p. 148—150° (from ethanol) (lit.,[5] 147—148°) (Found: C, 53·6; H, 5·9. Calc. for $C_{13}H_{16}ClNS,HCl$: C, 53·8; H, 5·9%)], *N*-2′-bromoethyl- [*hydrobromide*, m. p. 179—180° (from ethanol–ether) (79%) (Found: C, 41·6; H, 4·5; Br, 42·9. $C_{13}H_{16}BrNS,HBr$ requires C, 41·2; H, 4·5; Br, 42·2%)], and *N*-2′-iodoethyl-*N*-ethyl-3-thionaphthenylmethylamine [*hydriodide* (47%), m. p. 182·5—183·5 (decomp.) (from ethanol) (Found: C, 33·3; H, 3·4. $C_{13}H_{16}INS,HI$ requires C, 33·0; H, 3·6%)].

2-Thenylamine Derivatives.—Chloromethylation of redistilled thiophen, b. p. 82—84°, by Wiberg and McShane's method [11] gave 2-chloromethylthiophen (40%), b. p. 64—66°/12·5 mm., which on treatment with benzylamine by the method of Campbell *et al.*[12] gave *N*-benzyl-2-thenylamine, b. p. 120—122°/0·2 mm., and *N-benzyldi-2-thenylamine*, m. p. 79—80° (from ethanol) (Found: C, 67·6; H, 5·9. $C_{17}H_{17}NS_2$ requires C, 68·2; H, 5·7%). The method of Campbell *et al.*[12] was used to convert the *N*-benzyl-2-thenylamine into *N*-benzyl-*N*-2′-hydroxyethyl-2-thenylamine, b. p. 135—143°/0·05 mm. [hydrochloride, m. p. 147—149° (from ethanol–ether) (lit.,[12] 146—147°)]. The usual procedures then gave *N*-benzyl-*N*-2′-chloroethyl- [hydrochloride (77%), m. p. 177—178° (from ethanol) (lit.,[12] 177—178°)], *N*-benzyl-*N*-2′-bromoethyl- [*hydrobromide* (82%), m. p. 164·5—165·5° (from ethanol) (Found: C, 43·2; H, 4·4; Br, 39·9. $C_{14}H_{16}BrNS,HBr$ requires C, 43·0; H, 4·4; Br, 40·8%); *picrylsulphonate*, m. p. 145—146° (from chloroform) (Found: C, 39·4; H, 3·5. $C_{20}H_{19}BrN_4O_9S_2$ requires C, 39·8; H, 3·2%)], and *N*-benzyl-*N*-2′-iodoethyl-2-thenylamine [*hydriodide* (58%), m. p. 162—163° (from much ethanol) (Found: C, 35·1; H, 3·7; I, 52·8. $C_{14}H_{16}INS,HI$ requires C, 34·7; H, 3·5; I, 52·3%)].

Dibenamine and its Analogues. Dibenamine (from L. Light and Co. Ltd.) was recrystallised from ethanol to m. p. 192—194°. The corresponding alcohol, prepared by the method of Gump and Nikawitz,[13] had m. p. 42—43°, b. p. 135—145°/2·5 mm., and gave a *picrylsulphonate*, m. p. 147—148·5° (Found: C, 50·0; H, 4·0. $C_{22}H_{22}N_4O_{10}S$ requires C, 49·5; H, 4·1%), and was converted into the bromo-compound (63%), m. p. 177—179° (lit.,[13] 177—179°), by the action of phosphorus tribromide (Gump and Nikawitz [13] used hydrobromic acid), and into the iodo-compound (80%), m. p. 175—176·5° (lit.,[13] 178—179°), by the action of phosphorus tri-iodide (cf. Geissman *et al.*[14]) (Found: C, 40·4; H, 3·7; I, 52·7. Calc. for $C_{16}H_{19}IN,HI$: C, 40·1; H, 4·0; I, 53·0%).

Procedure.—This was as described in Part II.[6] The efficiency of the ether-extraction in removing unchanged halogenoalkylamine has been checked by appropriate halogen determinations. Hydroxyalkylamine has been shown not to interfere with the acidity titrations, and one of the less stable ethyleniminium ions has been shown to be unhydrolysed during the thiosulphate–iodine procedure for determination of ethyleniminium ion.

[10] Krasouskii, *J. Chem. Ukraine*, 1924, **1**, 398; cf. *Chem. Abs.*, 1926, **20**, 2820.
[11] Wiberg and McShane, *Org. Synth.*, 1949, **29**, 31.
[12] Campbell, Ackerman, and Campbell, *J. Amer. Chem. Soc.*, 1949, **71**, 2905; cf. U.S.P. 2,640,828, and *Chem. Abs.*, 1954, **49**, 4001.
[13] Gump and Nikawitz, *J. Amer. Chem. Soc.*, 1950, **72**, 1309.
[14] Geissman, Hochmann, and Fukuto, *J. Amer. Chem. Soc.*, 1952, **74**, 3313.

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FIG. 1.

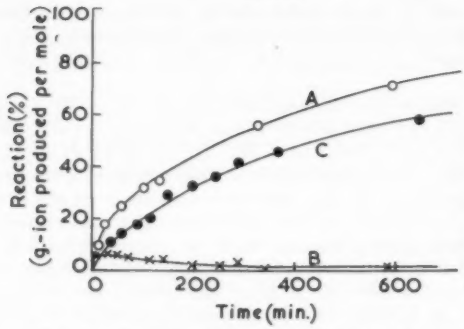


FIG. 2.

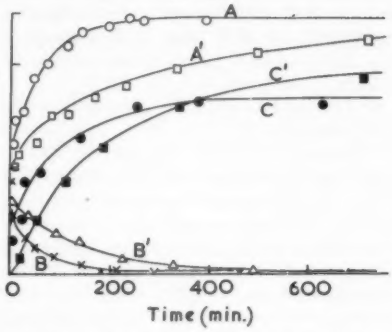


FIG. 1. *Decomposition of* N-2′-*chloroethyl*-N-*ethyl*-9-*fluorenylamine at* 30° *in aqueous acetone.*
A, *Chloride ion liberated.* B, *Ethyleniminium ion formed.* C, *Hydrogen ion formed.*

FIG. 2. *Decomposition of* N-2′-*bromoethyl*-N-*ethyl*-9-*fluorenylamine at* 30° *and at* 19° *in aqueous acetone.*
A,A′, *Bromide ion formed*; B,B′, *Ethyleniminium ion formed*; C,C′, *Hydrogen ion formed*; *at* 30° *and* 19° *respectively.*

FIG. 3.

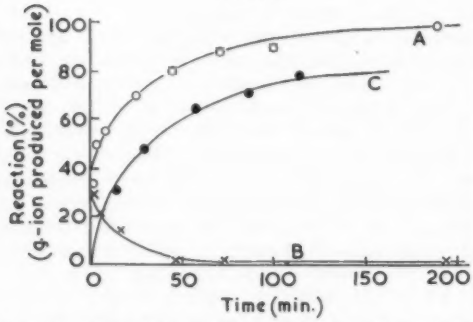


FIG. 4.

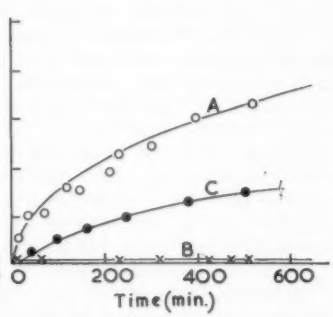
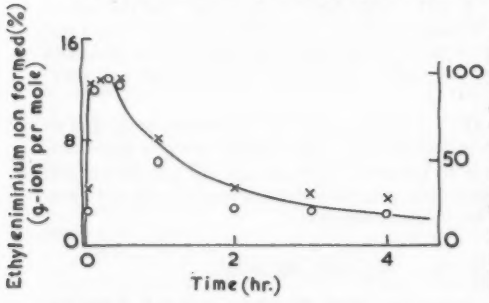
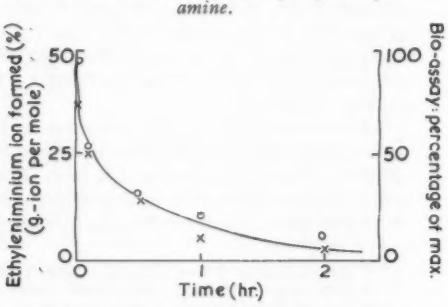


FIG. 3. *Decomposition of* N-2′-*bromoethyl*-N-*ethyl*-9-*fluorenylamine at* 37° *in aqueous acetone.*
FIG. 4. *Decomposition of* N-*benzyl*-N-2′-*bromoethyl*-9-*fluorenylamine at* 30° *in aqueous acetone.*
For Figs. 3 *and* 4: A, *bromide ion liberated.* B, *Ethyleniminium ion formed.* C, *Hydrogen ion formed.*

FIG. 5. N-2′-*Chloroethyl*-N-*ethyl*-9-*fluorenylamine.*

FIG. 6. N-2′-*Bromoethyl*-N-*ethyl*-9-*fluorenylamine.*





For Figs. 5 *and* 6: *The curve shows the concentration of ethyleniminium ion in in g.-ion per mole. Points represent bio-assays* (○) *against noradrenaline,* (×) *against adrenaline. Both refer to aqueous acetone solutions at* 30°.

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Discussion

It will be seen from Table 1 that the bromo- and iodo-compounds derived from *N*-ethyl-9-fluorenylamine are, on a molar basis, anti-adrenaline and anti-noradrenaline agents of extraordinary potency,[15] being some 10—20 times more active than the well-known substances Phenoxybenzamine (Dibenyline) and SY28. It seemed to us of particular interest therefore to study the reactivity of these compounds and some closely related ones, and in one or two cases, to try to relate the variation with time of the chemically determined ethyleniminium-ion concentrations with variation with time of the bio-assays of the ion based on anti-adrenaline and anti-noradrenaline activity. The results are displayed in Figs. 1—6.

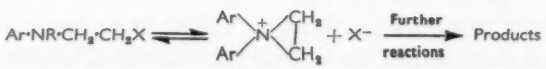
Comparison of Figs. 2 and 3 shows that for *N*-2′-bromoethyl-*N*-ethyl-9-fluorenylamine, the concentration of the related ethyleniminium ion at any time is little affected by increasing the temperature from 30°, at which most of our measurements have been made, to 37° which is approximately physiological. The overall rate of reaction of the halogeno-

Table 1. *Reactions and properties of* Ar·NR·CH_2·CH_2X,HX.

Compound			Propn. of X^- formed * (%) at 30° (after 360 min.)	Max. propn. of ethylen-iminium ion formed * (%) at 30°	Anti-adrenaline activity † (micromole/kg.)	Anti-nor-adrenaline activity † (micromole/kg.)
Ar	X	R				
9-Fluorenyl	Cl	Et	56	6·5	0·32	0·45
,,	Br	Et	100	36	0·06	0·10
,,	I	Et	88	14	0·03	0·04
,,	Cl	CH_2Ph	12·5	1	7·4	7·5
,,	Br	CH_2Ph	56	4	1·9	2·4
3-Thionaphthenyl-methyl	Cl	Et	58	22	1·4	1·9
,, ,,	Br	Et	93·5	72	1·6	2·6
,, ,,	I	Et	82	56	1·3	2·4
2-Thenyl	Cl	CH_2Ph	9	1·5	29·8	33·1
,,	Br	CH_2Ph	71·5	10	2·4	19·7
,,	I	CH_2Ph	35	4	1·2	2·2
9-Fluorenyl §	Cl	Et	78	4	2·6	4·3
,, §	Br	Et	99·5	31	0·06	0·06
Benzyl	Cl	CH_2Ph	12	2	10 ‡	—
,,	Br	CH_2Ph	78	16	5 ‡	—
,,	I	CH_2Ph	38	4·5	—	—
SY28 [a]			100	86	0·75	0·98
Dibenyline [b]	—	—	—	—	0·40	0·49

* G.-ion/mole. † E.D. 50 in spinal rats. ‡ Ref. 13. § Side chain is CHMe·CH_2X,HX.
[a] 1-$C_{10}H_7$·CH_2·NEt·CH_2·CH_2Cl,HCl. [b] PhO·CH_2·CHMe·N(CH_2Ph)·CH_2·CH_2Cl,HCl.

amine increases noticeably on so increasing the temperature, as would be expected, and the limited effect on the ethyleniminium-ion concentration must be due to a balance of increased rate of formation and of decomposition. Figs. 5 and 6 show that with these very active fluorenylamine derivatives, there is the same proportionality between ethyleniminium-ion concentration and anti-adrenaline activity as has been observed with other groups of compounds.[15] The general pattern of the decomposition as exemplified in Figs. 1—4 conforms with previous observations in this field, and is interpreted in terms of the scheme:



It is clear that hydrolysis is the predominant mode of further reaction of the ethyleniminium ion, but it is probable that significant amounts of halogeno-amine are consumed by reaction with the ion to yield piperazinium salts. Pharmacological testing of appropriately aged

[15] Graham, (*a*) *Brit. J. Pharmacol.*, 1957, **12**, 489; (*b*) *J. Med. Pharm. Chem.*, 1960, **2**, 911.

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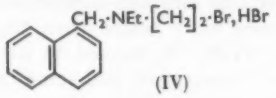
solutions has again shown that these salts are inactive against adrenaline and noradrenaline (cf. Part III [16]). In the fluorenylamine group, replacement of an *N*-ethyl radical by a *N*-benzyl radical depresses reactivity and anti-adrenaline activity (Table 1).



(IV)

(V) H NEt·[CH₂]₂·Br,HBr

The change of structure from (IV) to (V) is associated with increased anti-adrenaline activity, but diminished reactivity. It is unfortunate that the related ethyleniminium

FIG. 7.

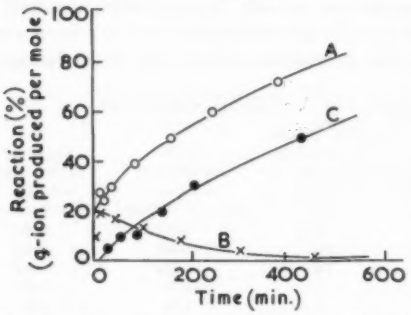


FIG. 8.

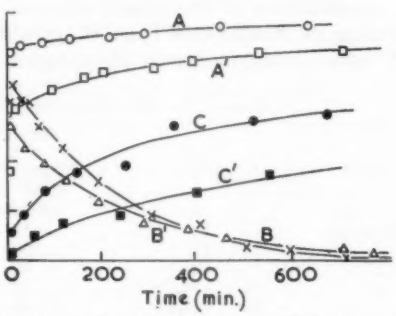


FIG. 7. *Decomposition of* N-2′-*chloroethyl*-N-*ethyl*-3-*thionaphthenylmethylamine at* 37° *in aqueous acetone.*

FIG. 8. *Decomposition of* N-2′-*bromoethyl*-N-*ethyl*-3-*thionaphthenylmethylamine and the corresponding iodo-compound at* 30° *in aqueous acetone.* A′, *Iodide ion liberated.* B′, *Ethyleniminium ion formed.* C′, *Hydrogen ion formed.*

FIG. 9.

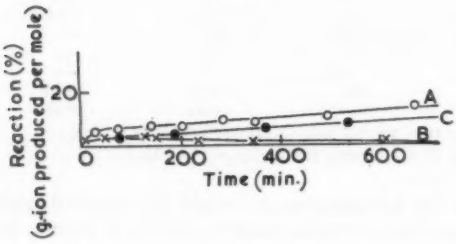


FIG. 10.

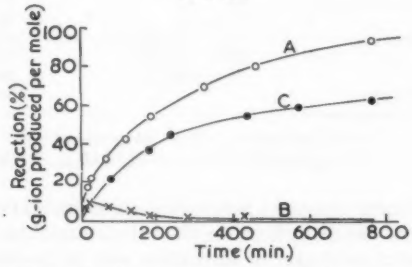


FIG. 9. *Decomposition of* N-*benzyl*-N-2′-*chloroethyl*-2-*thenylamine at* 30° *in aqueous acetone.*

FIG. 10. *Decomposition of* N-*benzyl*-N-2′-*bromoethyl*-2-*thenylamine at* 30° *in aqueous acetone.*

For Figs. 7 *and* 9: A, *Chloride ion liberated.* B, *Ethyleniminium ion formed.* C, *Hydrogen ion formed.*
For Figs. 8 *and* 10: A, *Bromide ion liberated.* B, *Ethyleniminium ion formed.* C, *Hydrogen ion formed.*

picrylsulphonates have either not been prepared, despite much effort, or are too insoluble for pharmacological study, so that the intrinsic pharmacological properties of the ions are unknown. Nevertheless, given that compound (IV) yields its ethyleniminium ion more rapidly and extensively than does (V), it appears very probable that the 9-fluorenyl group is associated with remarkably high intrinsic anti-adrenaline properties. Belleau [17] has

[16] Chapman and Allen, *J.*, 1960, 1482.
[17] Belleau, *Canad. J. Biochem. Physiol.*, 1958, **36**, 731.

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explained this in terms of the relative basicities of the naphthalene and fluorene nuclei, but possibly the flatness, area, and compactness of the fluorene nucleus are also relevant.

The results assembled in Table 1 and in Figs. 7—10 relate to the effect of isosteric replacement of two aromatic carbon atoms by a sulphur atom on the phenomena under investigation. Considering the thionaphthenylmethyl derivatives in relation to the 1-naphthylmethyl derivatives previously reported (Part II [6]) some divergencies of pattern emerge. With 1-naphthylmethyl derivatives the maximum proportion of ethyleniminium ion produced is in the order $I > Br > Cl$, whereas with thionaphthenylmethyl derivatives the order is $Br > I > Cl$. As to anti-adrenaline activities these show the orders $Cl \approx Br > I$ for 1-naphthylmethyl compounds and $Cl \approx Br \approx I$ for thionaphthenylmethyl compounds. The outstanding feature of both of these groups of compounds is the almost equal anti-adrenaline activity of the chloro-, bromo-, and iodo-compounds, whereas with fluorenyl-, chlorobenzyl-, dibenzyl-, and benzyl-thenyl derivatives the chloro-compounds are significantly less active. We can offer no explanation of this at present.

On isosteric replacement in dibenamine and its bromo- and iodo-analogues, the pattern of reactivity is in this case largely unaltered and, after allowance for the fact that the pharmacological results are not exactly comparable, so is that of anti-adrenaline activity.

Chapman and James [6] previously reported that dibenamine in aqueous acetone (1 : 2) at 30° gave negligible amounts of ethyleniminium ion. Careful re-investigation of this compound and related compounds has revealed small but measurable amounts of ethyleniminium ion in these solutions. Harvey and Nickerson,[7] working with aqueous ethanol solutions, also found by an indirect method small amounts of ethyleniminium ion. We have re-investigated this system, using a different and more direct technique than that of Harvey and Nickerson [7] and confirm their observations qualitatively, but find quantitative differences both as to chloride and ethyleniminium-ion concentrations. The differences as to ethyleniminium-ion concentration are small in absolute magnitude, but in our view significant and beyond the limits of experimental error in this work. The relevant results are assembled in Table 2. It is clear from these results that aqueous ethanol is a more

TABLE 2. *Decomposition of dibenamine (free base) at 27° and 37°.*

Propn. of Cl^- liberated * at 27° after 800 min.		Max. propn. of ethyleniminium ion produced * at 27°	
70% Aq. EtOH	2 : 1 Acetone–water	70% Aq. EtOH	2 : 1 Acetone–water
60%	20%	4%	2%
68% †	—	5% ‡	—
		10% §	—
At 37° after 400 min.		At 37°	
65%	27%	2%	2%
90%	—	5% ‡	—
		8% §	—

* G.-ion/mole. † After 400 min. ‡ Determined by thiosulphate consumption. § Determined by Harvey and Nickerson's method.[7]

favourable solvent for the decomposition of halogenoethylamines by an internal S_N2 process than is aqueous acetone. Harvey and Nickerson [7] used an excess of sodium hydrogen carbonate for the liberation of the free base from the hydrochloride, whereas we have used one equivalent of sodium hydroxide. We have shown that this leads to significant differences in the chloride ion figures.

We thank the University of Southampton for a research studentship (to A. J. T.) and Imperial Chemical Industries Limited and The Chemical Society for a grant for materials. The collaboration of Dr. J. D. P. Graham and colleagues is gratefully acknowledged.

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[*Received, September 26th,* 1960.]

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251. *Pyrimidine Reactions. Part III.*[1] *The Methylation Product of 4-Amino-6-hydroxypyrimidine, and Related Compounds.*

By D. J. Brown and J. S. Harper.

Methylation of 4-amino-6-hydroxypyrimidine is rigorously proved to occur at $N_{(1)}$, and a substance recently described by others as the 3-methyl derivative is shown to have rearranged to 4-hydroxy-6-methylamino-pyrimidine during preparation. Derived purines and pteridines are described. 4-Hydroxy-6-methylthio- and 4-chloro-6-hydroxy-pyrimidine are shown to be methylated also on the ring-nitrogen atom that stands α to the hydroxy-group, although a little methoxy-derivative is also formed in the first case. A variety of the $N_{(4)}$- and *O*-methylated derivatives of 4-amino-6-hydroxypyrimidine, of related compounds, and of dithiouracil are recorded. The ionisation constants are discussed.

Although a great many methylated pyrimidines bearing two tautomeric groups in positions 2 and 4 are known, relatively few of the analogous 4,6-disubstituted derivatives have been made. This paper mainly describes methylation products theoretically derivable from 4-amino-6-hydroxypyrimidine (I; R = NH_2) and examples of their use in preparing purines and pteridines required in connexion with mammalian xanthine oxidase studies.[2]

Treatment of 4-amino-6-hydroxypyrimidine with dimethyl sulphate and alkali gives a single methylated derivative formulated[3] as 4-amino-1,6-dihydro-1-methyl-6-oxo-pyrimidine (II; R = NH_2) because it can be also made by desulphurising its 2-methylthio-derivative. However, this evidence is inadmissible because the structure of the methyl-thio-derivative is in fact unproved.[4] Moreover, contrary to published data, the 3-methylated isomer of (II; R = NH_2) is still unknown (see below) and cannot therefore be invoked in a process of elimination. The structure of the methylation product as (II; R = NH_2) was therefore proved as follows: its 5-nitro-derivative (III; R = NO_2) was catalytically reduced to 4,5-diamino-1,6-dihydro-1-methyl-6-oxopyrimidine (III; R = NH_2), and condensation with glyoxal gave a pteridine identified by direct comparison as 3,4-dihydro-3-methyl-4-oxopteridine[5] (IV; R = H). The 3,6,7-trimethyl analogue (IV; R = Me) was similarly made, and fusion of the diamino-derivative (III; R = NH_2) with urea and thiourea then gave 1,6-dihydro-8-hydroxy-1-methyl-6-oxopurine (V; R = OH) and its 8-mercapto-analogue (V; R = SH) respectively. A related synthesis of 6,8-dihydroxy-9-methylpurine (previously made indirectly by Fischer and Ach[6]) is also described below.

6-Amino-1,4-dihydro-1-methyl-4-oxopyrimidine (VI; R = H), isomeric with the methylation product of 4-amino-6-hydroxypyrimidine, has been assumed[3] as the structure of the product obtained by desulphurising the 2-mercapto-derivative[7] (VI; R = SH) with Raney nickel. However, the close similarity in ultraviolet spectra[3] of the desulphurisation product and its isomer (II; R = NH_2) is puzzling if the former is really represented by (VI; R = H). On the other hand, if the possible rearrangement[8] to (VII) had occurred, the spectral coincidence would be reasonable. Accordingly, the desulphurisation product was prepared, and direct comparison with an authentic specimen[9] of (VII), showed them identical. Since the structure of the thiol (VI; R = SH) has been indirectly proved by Elion,[10] and moreover its *S*-methylated derivative (VI; R = SMe) shows no acidic properties, rearrangement must have taken place during desulphurisation.

[1] Part II, *J.*, 1959, 3647.
[2] Bergmann, Kwientny, Levin, and Brown, *J. Amer. Chem. Soc.*, 1960, **82**, 598.
[3] Pfleiderer and Liedek, *Annalen*, 1958, **612**, 163.
[4] Johns and Hendrix, *J. Biol. Chem.*, 1915, **20**, 153.
[5] Albert, Brown, and Wood, *J.*, 1956, 2066.
[6] Fischer and Ach, *Ber.*, 1899, **32**, 250.
[7] Traube and Winter, *Arch. Pharm.*, 1906, **244**, 11; through *Chem. Zentr.*, 1906, I, 1336.
[8] Brown, *Nature*, 1961, in the press, and bibliography therein.
[9] Brown, *J. Appl. Chem.*, 1955, **5**, 358.
[10] Elion, in the Ciba Symposium, "The Chemistry and Biology of Purines," Churchill Ltd., London, 1957, p. 39.

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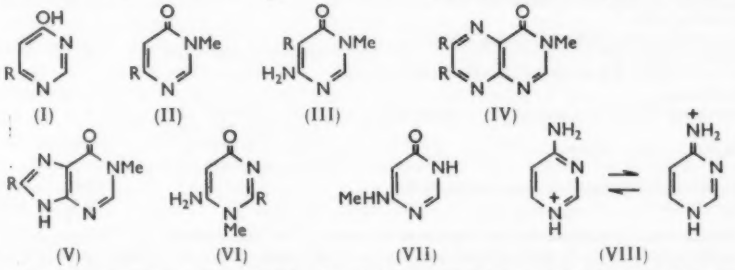
Attempted gentle desulphurisation of the sulphide (VI; R = SMe) in ethanol failed to yield the missing isomer (VI; R = H).

The syntheses of other methylated analogues of the pyrimidines (I) and (II) were approached through 4,6-dichloropyrimidine.[11] Partial hydrolysis in acid gave 4-chloro-6-hydroxypyrimidine (I; R = Cl) which has been previously made only indirectly. With diazomethane this gave two products. The minor one was identical with the recently described [12] 4-chloro-6-methoxypyrimidine. The major one was identified as 4-chloro-1,6-dihydro-1-methyl-6-oxopyrimidine (II; R = Cl) when it was converted by ammonia into the amine (II; R = NH_2). Mono- and di-methylamine likewise gave analogues (II; R = NHMe and NMe_2). Methylation of 4-hydroxy-6-methylthiopyrimidine [12] (I; R = SMe) gave a single *N*-methyl derivative shown to be 1,6-dihydro-1-methyl-4-methylthio-6-oxopyrimidine (II; R = SMe) by conversion into the above base (II; R = NMe_2). Preparation by conventional routes of other methylated derivatives of the amine (I; R = NH_2) starting from 4,6-dichloropyrimidine or 4-chloro-6-hydroxypyrimidine (I; R = Cl), and of related and derived compounds, is described in the Experimental section. Several known compounds appear therein because an improved route to each has been used, and some new methylated derivatives of dithiouracil are also included. Among these is 1,2,3,4-tetrahydro-1,3-dimethyl-2,4-dithiopyrimidine, prepared by vigorous thiation of *NN'*-dimethyluracil. Although much gentler conditions have been claimed by Klingsberg and Papa [13] to yield this dithio-derivative, repetition revealed that their product had the analysis, m. p., and spectrum of the known [14] monothiated, 1,3-dimethyl-4-thiouracil.



The ionisation constants recorded in the Table provide some insight into factors affecting basic and acidic strength in pyrimidines. The basic nature of pyrimidine, whose pK_a 1·3 is strikingly lower [15] than that of pyridine (5·2), is usually assumed to result from a depletion of π-electrons by the second nitrogen atom. If this is true, 3-nitropyridine which contains a similarly placed and strongly electron-attracting centre, should approximate to pyrimidine in pK_a. In fact, the value now determined (0·8) supports this hypothesis. Insertion of a 4-amino-group into pyrimidine might be expected to increase basic strength by only one unit of pK_a, as is seen in passing from aniline to the diaminobenzenes, but 4-aminopyrimidine is a much stronger base [15] (pK_a 5·7) because it has a strongly resonance-stabilised cation (VIII). The base-weakening effect of an electron-withdrawing group on 4-aminopyrimidine is seen in 4-amino-6-chloropyrimidine (2·1) and its analogues, and in comparing 4,6-diaminopyrimidine (6·0) with its 5-bromo-derivative (4·2). The normal small base-strengthening effect of an electron-releasing group applies in 4,6-diaminopyrimidine and in its extranuclear methylated derivatives, but the introduction of an oxo- or " hydroxy "-group (always in the oxo-form,[16]) at once destroys the basis of 4-aminopyrimidine's basic strength by rearranging the double bonds to exclude a cation

[11] Hull, *J.*, 1951, 2214.
[12] Isbecque, Promel, Quinaux, and Martin, *Helv. Chim. Acta*, 1959, **42**, 1317.
[13] Klingsberg and Papa, U.S.P. 2,676,969/1954.
[14] Elion and Hitchings, *J. Amer. Chem. Soc.*, 1947, **69**, 2138.
[15] Albert, Goldacre, and Phillips, *J.*, 1948, 2240.
[16] Brown, Hoerger, and Mason, *J.*, 1955, 211.

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Pyrimidine derivative	pK_a[a] spread (in parentheses), and concn. (10^{-3}M) (in square brackets) acidic	basic
4-Amino-6-hydroxy-	10·05 (±0·03) [10]	1·36 (±0·04) [50]
4-Amino-6-methoxy-	—	4·02 (±0·06) [5]
4-Hydroxy-6-methylamino-[b]	10·47 (±0·02) [5]	<1·7
4-Dimethylamino-6-hydroxy-	10·42 (±0·03) [50]	1·22 (±0·03) [50]
4-Methoxy-6-methylamino-	—	4·23 (±0·03) [5]
4-Dimethylamino-6-methoxy-	—	4·29 (±0·04) [5]
4-Amino-1,6-dihydro-1-methyl-6-oxo-[c]	—	0·98 (±0·03) [50]
1,6-Dihydro-1-methyl-4-methylamino-6-oxo-	—	<1
1,6-Dihydro-4-dimethylamino-1-methyl-6-oxo-	—	<1
6-Amino-1-methyl-2-thiouracil	9·84 (±0·05)[d]	0·0 (±0·08)[d]
4-Hydroxy-6-mercapto-	4·33 (±0·03) [5]	—
	10·52 (±0·06) [5]	
4-Hydroxy-6-methylthio-	8·52 (±0·01) [5]	—
Di(4-hydroxypyrimidin-6-yl) sulphide	7·20 (±0·02) [2·5]	—
	8·48 (±0·02) [2·5]	
4-Amino-6-chloro-	—	2·10 (±0·02) [5]
4-Chloro-6-methylamino-	—	2·24 (±0·03) [5]
4-Chloro-6-dimethylamino-	—	2·42 (±0·05) [5]
4-Chloro-6-hydroxy-	7·43 (±0·03) [2]	—
4,6-Diamino-	—	6·01 (±0·04) [2]
4-Amino-6-methylamino-	—	6·32[e]
4,6-Bismethylamino-	—	6·39 (±0·05) [50]
4-Dimethylamino-6-methylamino-	—	6·39 (±0·03) [5]
4,6-Bisdimethylamino-	—	6·36 (±0·02) [5]
4,6-Diamino-5-bromo-	—	4·22 (±0·02) [2·5]
4,5-Diamino-1,6-dihydro-1-methyl-6-oxo-	—	3·46 (±0·02) [20]
2,4-Bismethylthio-[b]	—	—
1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dithio-[b]	—	—
1-Methyldithiouracil[b]	7·47 (±0·05) [0·5]	—
1,2,3,4-Tetrahydro-1,3-dimethyl-2-oxo-4-thio-[b]	—	—
Other compounds		
1,6-Dihydro-8-hydroxy-1-methyl-6-oxopurine[b]	8·52 (±0·02) [2·5]	<2
	11·83 (±0·04) [2·5]	
6,8-Dihydroxy-9-methylpurine[b]	8·31 (±0·01) [5]	<1·5
	11·74 (±0·04) [5]	
3,4-Dihydro-3,6,7-trimethyl-4-oxopteridine[b]	—	−0·05 (±0·05)
3-Nitropyridine[f]	—	0·77 (±0·04) [50]

[a] Determined by potentiometric titration in water at 20° (cf. Albert and Phillips, *J.*, 1956, 1294). [b] Ultraviolet spectra in Experimental section. [c] Light absorption as neutral molecule at pH 4·8, $\lambda_{max.}$ 257, 216 (log ε 3·80, 4·54). [d] Spectrophotometric determination. [e] From Brown and Jacobsen, *J.*, 1960, 1978. [f] Prepared as by den Hertog and Overhoff, *Rec. Trav. chim.*, 1930, **49**, 552. Bryson, *J. Amer. Chem. Soc.*, 1960, **82**, 4871, gives pK_a 0·81 at 25°.

stabilised as is (VIII). Thus 4-amino-6-hydroxypyrimidine (pK_a 1·4) and its 1-methyl derivative have basic strengths of the order of pyrimidine. Naturally, when the "hydroxy"-configuration is preserved by *O*-methylation, basic strength does not suffer in this way, so that 4-amino-6-methoxypyrimidine and its analogues have pK_a values above 4.

The acidic strength of 4-hydroxypyrimidine (pK_a 8·6) is increased as usual by the electron-withdrawing chloro-group (4-chloro-6-hydroxypyrimidine; pK_a 7·4), and weakened by the electron-releasing amino- or dimethylamino-group (4-amino-6-hydroxypyrimidine; pK_a 10·0). The acidic values for di-(4-hydroxypyrimidin-6-yl) sulphide (7·2 and 8·5) are interesting in that the equivalent ionising centres are neither far enough apart in space to give the same figure, nor yet close enough for the formation of the first anion to affect profoundly the second figure.

Experimental

Analyses are by Dr. J. E. Fildes and her staff.

4-Amino-1,6-dihydro-1-methyl-5-nitro-6-oxopyrimidine.—Nitric acid (*d* 1·5; 27 ml.) was slowly added with stirring to 4-amino-1,6-dihydro-1-methyl-6-oxopyrimidine[3] (18·2 g.) dissolved in concentrated sulphuric acid (55 ml.), kept at 35—40° during the addition and for a further 30 min. The mixture was poured on ice (400 g.), and the solid (20·8 g.) recrystallised

from water (90 parts), giving the *nitro-compound*, m. p. 184° (Found: C, 35·3; H, 3·4. $C_5H_6N_4O_3$ requires C, 35·3; H, 3·55%).

4,5-Diamino-1,6-dihydro-1-methyl-6-oxopyrimidine.—The above nitro-compound (18·3 g.), suspended in methanol (500 ml.), was hydrogenated over Raney nickel. The catalyst was filtered off and extracted with boiling water (50 ml.). The residue from evaporation of the combined filtrates was twice recrystallised (with concentration) from ethanol (25 parts), giving the *diamine* (7 g.), m. p. 193° (Found: N, 40·0. $C_5H_8N_4O$ requires N, 40·0%).

3,4-Dihydro-3-methyl-4-oxopteridine.—The pyrimidine-diamine (0·25 g.) was refluxed for 30 min. with polygloxal (0·25 g.) in methanol (5 ml.). After removal of solvent and successive recrystallisation from water and ethanol, the material was identical (mixed m. p. and chromatography) with the authentic [5] pteridine.

3,4-Dihydro-3,6,7-trimethyl-4-oxopteridine.—The diamine (0·5 g.), biacetyl (0·5 g.), and water (1 ml.) were heated at 95° for 30 min., then evaporated to dryness. Recrystallisation from ethanol (25 parts) gave the *oxopteridine*, m. p. 241° (Found: C, 56·8; H, 5·3; N, 29·4. $C_9H_{10}N_4O$ requires C, 56·8; H, 5·3; N, 29·45%), $\lambda_{max.}$ (at pH 7) 312, 282sh, 238 (log ε 3·89, 3·67, 4·13).

1,6-Dihydro-8-hydroxy(and -mercapto)-1-methyl-6-oxopurine.—A mixture of the diamine (0·5 g.) and urea (0·5 g.) was fused at 175° for 5 min. The residue was adjusted to pH 5—6 during recrystallisation from water (125 parts), to give the *hydroxypurine* (0·4 g.), m. p. *ca.* 415° (Found, for material dried at 170°: N, 33·55. $C_6H_6N_4O_2$ requires N, 33·7%). Light absorption as monoanion at pH 10·18, $\lambda_{max.}$ 274 (log ε 4·11); as neutral molecule at pH 4·7, $\lambda_{max.}$ 259 (log ε 4·10).

Made similarly with thiourea at 210°, and twice reprecipitated with acetic acid from warm dilute soda, the *mercapto-analogue* (0·48 g.) did not melt below 360° (Found: C, 39·8; H, 3·5; N, 30·6. $C_6H_6N_4OS$ requires C, 39·55; H, 3·3; N, 30·75%).

6,8-Dihydroxy-9-methylpurine.—5-Amino-4-hydroxy-6-methylaminopyrimidine [9] was fused with urea as for the above hydroxypurine. The product (80%), recrystallised from water, did not melt below 360° and corresponded to Fischer and Ach's product [6] in solubilities (Found: N, 33·5. Calc. for $C_6H_6N_4O_2$: N, 33·7%). Light absorption as monoanion at pH 9·94, $\lambda_{max.}$ 264 (log ε 4·12); as neutral molecule at pH 4·7, $\lambda_{max.}$ 259 (log ε 4·12).

4-Hydroxy-6-methylaminopyrimidine.—Desulphurisation [3] of 6-amino-1-methyl-2-thiouracil [7] gave the product of m. p. 251°, undepressed on admixture with 4-hydroxy-6-methylaminopyrimidine [9] (Found: C, 47·75; H, 5·8; N, 33·4. Calc. for $C_5H_7N_3O$: C, 48·0; H, 5·65; N, 33·55%). The specimens gave identical paper chromatograms in each of three solvents and agreed in ultraviolet spectrum as neutral molecules in water at pH 4·8 ($\lambda_{max.}$ 261, 219; log ε 4·06, 4·40).

6-Amino-1,4-dihydro-1-methyl-2-methylthio-4-oxopyrimidine.—6-Amino-1-methyl-2-thiouracil [7] (0·8 g.) in N-potassium hydroxide (5·5 ml.) was shaken with methyl iodide (0·4 ml.) for 20 min. The *methylthio-derivative* (0·6 g.), after recrystallisation from water (10 ml.), had m. p. 272° (decomp.) (Found: C, 42·2; H, 5·35; N, 24·5. $C_6H_9N_3OS$ requires C, 42·1; H, 5·3; N, 24·55%). It was insoluble in aqueous sodium hydroxide.

4-Chloro-6-hydroxypyrimidine.—4,6-Dichloropyrimidine [11] (38·5 g.) was stirred on the steam-bath for 1 hr. with 3N-hydrochloric acid (510 ml.). The mixture was adjusted to pH 9—10 with ammonia (*d* 0·91; *ca.* 170 ml.) and treated with carbon and kieselguhr. The filtrate was acidified to pH 2—3, to give the chlorohydroxypyrimidine (21 g.), which, recrystallised from ethanol (12 parts), had m. p. 192—193° (lit.,[12] 192—193°) (Found: C, 36·9; H, 2·4; N, 21·5. Calc. for $C_4H_3ClN_2O$: C, 36·8; H, 2·3; N, 21·5%).

4-Chloro-1,6-dihydro-1-methyl-6-oxopyrimidine.—4-Chloro-6-hydroxypyrimidine (27·2 g.) was added slowly to ethereal diazomethane (from 100 g. of nitrosomethylurea). Next morning, the residue from evaporation was twice recrystallised from light petroleum (b. p. 80—100°; 3 l. and 1·1 l.) giving the *1-methylpyrimidine* (28%), m. p. 87—88° (Found: N, 19·3. $C_5H_5ClN_2O$ requires N, 19·4%). Distillation of the mother-liquors from the first recrystallisation gave an oily residue which was dissolved in ether and treated with carbon; the ether was allowed to evaporate in air. After several days, the solid was removed and the oil fractionally distilled, to give 4-chloro-6-methoxypyrimidine (2·6%), b. p. 80° (18 mm.). The ultraviolet spectrum and m. p. (29°) agreed with published figures.[12]

The 1-methyl derivative (1 g.) and 7% ethanolic ammonia (6 ml.) were heated at 140° for 2 hr. Evaporation and removal of ammonium chloride by trituration with water (2 ml.) gave

4-amino-1,6-dihydro-1-methyl-6-oxopyrimidine (0·3 g.), identified by mixed m. p. and paper chromatography.

1,6-Dihydro-1-methyl-4-methylamino- and 4-Dimethylamino-1,6-dihydro-1-methyl-6-oxopyrimidine.—4-Chloro-1,6-dihydro-1-methyl-6-oxopyrimidine (1 g.) and 33% w/w ethanolic methylamine (4 ml.) were kept at 25° for 24 hr. The residue after evaporation was added to methanol (10 ml.) with which sodium (0·14 g.) had reacted. The solution was reduced to 10 ml. *in vacuo* to remove the excess of amine and adjusted to pH 3—4 with hydrochloric acid. The residue after evaporation was extracted with boiling isobutyl methyl ketone (2 × 15 ml.) and treated with carbon. The *methylamino-derivative* (0·3 g.), when recrystallised from the ketone, had m. p. 187—188° (Found: C, 51·9; H, 6·6; N, 30·1. $C_6H_9N_3O$ requires C, 51·8; H, 6·5; N, 30·2%). Made similarly, the crude *dimethylamino-analogue* (0·5 g.) was sublimed *in vacuo*, and recrystallised from ethyl acetate, and then had m. p. 156—157° (Found: C, 55·35; H, 7·3; N, 27·4. $C_7H_{11}N_3O$ requires C, 54·9; H, 7·25; N, 27·4%). It was also made in small yield by treating 1,6-dihydro-1-methyl-4-methylthio-6-oxopyrimidine with dimethylamine at 110°, and identified by mixed m. p. and chromatography.

1,6-Dihydro-1-methyl-4-methylthio-6-oxopyrimidine.—A shaken solution of 4-hydroxy-6-methylthiopyrimidine [12] (3·25 g.) in 2N-potassium hydroxide (13 ml.) at 20° was treated with dimethyl sulphate (5 × 0·5 ml.) at 10 min. intervals, then shaken for 90 min. longer. Refrigeration gave a solid (3·3 g.) which was twice recrystallised from 15 ml. of a 1 : 1 mixture of 0·1M-sodium carbonate and 0·1M-sodium hydrogen carbonate, to remove a little starting material. The *oxopyrimidine*, crystallised from ethanol (13 parts), had m. p. 172—175° (Found: C, 45·8; H, 4·95; N, 17·9. $C_6H_8N_2OS$ requires C, 46·15; H, 5·15; N, 17·95%).

4-Amino-6-chloropyrimidine.—4,6-Dichloropyrimidine (16 g.) and 8% ethanolic ammonia (72 ml.) were heated at 100° for 1 hr. Refrigeration, and recrystallisation of the resulting solid from water (500 ml.), gave 60% of aminochloropyrimidine, m. p. 204—205° (lit.,[17] 215°) (Found: C, 36·8; H, 3·05; N, 32·45. Calc. for C H_4ClN_3: C, 37·05; H, 3·1; N, 32·4%).

4-Amino-6-methoxypyrimidine.—A suspension of the preceding chloro-amine (2·6 g.) in methanolic sodium methoxide (0·7 g. of sodium) was stirred under reflux for 90 min. Carbon dioxide was then led in, and the whole evaporated to dryness. Sublimation (85°/0·05 mm.) gave the aminomethoxypyrimidine (96%), m. p. 150—151° (lit.,[3] 156—157°) (Found: C, 47·7; H, 5·6; N, 33·6. Calc. for $C_5H_7ON_3$: C, 48·0; H, 5·6; N, 33·6%).

4-Chloro-6-dimethylaminopyrimidine.—4,6-Dichloropyrimidine (10·45 g.) and 33% w/w ethanolic dimethylamine (36·5 ml.) were shaken for 2 hr. at 25°. The *pyrimidine* (6·85 g.), recrystallised from water (55 parts), or sublimed (70°/0·05 mm.), had m. p. 102—103° (Found: C, 45·5; H, 5·05; N, 26·75. $C_6H_8ClN_3$ requires C, 45·7; H, 5·1; N, 26·65%).

4-Dimethylamino-6-methoxy(and -hydroxy)pyrimidine.—The last-mentioned compound (10 g.) was stirred for 90 min. in refluxing methanolic sodium methoxide (50 ml.; sodium, 2·2 g.). After treatment with carbon dioxide and evaporation, the residual paste was extracted (Soxhlet) with light petroleum (b. p. 40—60°). Removal of solvent and distillation gave the *methoxy-derivative* (6·3 g.), b. p. 136° (20 mm.), n_D^{20} 1·5418 (Found: C, 54·4; H, 7·25; N, 27·4. $C_7H_{11}N_3O$ requires C, 54·9; H, 7·25; N, 27·4%). This product (6 g.) was refluxed for 30 min. with 6N-hydrochloric acid. After evaporation to dryness, the residue was dissolved in hot water (6 ml.) and adjusted to pH 7. The resulting *hydroxy-derivative* (2·1 g.), recrystallised from water (*ca.* 20 parts), had m. p. 271—275° (decomp.) (Found, in sample dried at 140°: C, 51·5; H, 6·55; N, 30·25. $C_6H_9ON_3$ requires C, 51·8; H, 6·5; N, 30·2%).

4-Dimethylamino-6-methylaminopyrimidine.—4-Chloro-6-dimethylaminopyrimidine (1·58 g.) and 25% w/v aqueous methylamine (3·8 ml.) were heated at 170° for 4 hr. After evaporation, the residue was extracted with boiling ethyl acetate (3 × 25 ml.). The solvent was removed and sublimation (80°/0·05 mm.) gave the *diamine* (1·2 g.), which, recrystallised from ethyl acetate (12 parts), had m. p. 138—141° (Found: C, 55·0; H, 7·85; N, 36·8. $C_7H_{12}N_4$ requires C, 55·25; H, 7·95; N, 36·8%).

4,6-Bisdimethylaminopyrimidine.—The solution obtained by heating 4,6-dichloropyrimidine (3·0 g.) with aqueous 25% w/v dimethylamine (21·7 ml.) for 4 hr. at 170° was extracted with ether (7 × 30 ml.). The solid (3·3 g.) left on evaporation of the extract recrystallised (with concentration) from light petroleum (b. p. 80—100°; 80 ml.); on sublimation, the *bisdimethylaminopyrimidine* had m. p. 107·5° (Found: C, 57·8; H, 8·3; N, 33·55. $C_8H_{14}N_4$ requires C, 57·8; H, 8·5; N, 33·7%).

[17] Whitehead and Traverso, *J. Amer. Chem. Soc.*, 1958, **80**, 2185.

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4,6-*Dimethoxypyrimidine*.—4,6-Dichloropyrimidine (3·0 g.) was refluxed for 90 min. with sodium methoxide (sodium, 1·4 g.) in methanol (35 ml.). The solution was treated with carbon dioxide and evaporated (without a vacuum) to an oil, which was extracted with light petroleum (b. p. 40—60°; 4 × 100 ml.). Removal of the solvent and distillation gave the *dimethoxypyrimidine* (0·75 g.), b. p. 85°/16 mm., and n_D^{20} 1·4980 (Found: C, 51·85; H, 6·0; N, 20·1. $C_6H_8N_2O_2$ requires C, 51·4; H, 5·75; N, 20·0%).

4,6-*Diamino-5-bromo- and* 4-*Amino-5-bromo-6-hydroxy-pyrimidine*.—Bromine (1·6 ml.) was added during 10 min. to a stirred suspension of 4,6-diaminopyrimidine [18] (3 g.) in water (30 ml.). After 30 min. the solution was adjusted to pH 9. The *bromo-diamine* (5·1 g.), recrystallised from water (80 parts), had m. p. 213° (Found: Br, 42·35; N, 29·5. $C_4H_5BrN_4$ requires Br, 42·3; N, 29·6%).

The *aminobromohydroxypyrimidine* was similarly made in 90% yield; recrystallised from water (*ca.* 30 parts) it had m. p. 268° (Found: C, 25·1; H, 2·3. $C_4H_4BrN_3O$ requires C, 25·1; H, 2·15%).

5-Bromocytosine was also made in 65% yield as above, except that about 12 hr. was needed for bromine-uptake. It had m. p. 240—242° (decomp.; lit.,[19] 235°) (Found: N, 22·0. Calc. for $C_4H_4BrN_3O$: N, 22·1%). Amination of this with 33% aqueous methylamine (10 parts) at 150° or 180° gave a small yield of 5-methylaminouracil, m. p. 290° (decomp.) (lit.,[20] 240° and 280°) (Found: N, 29·8. Calc. for $C_5H_7N_3O_2$: N, 29·8%).

Di-(4-*hydroxypyrimidin*-6-*yl*) *Sulphide*.—4-Chloro-6-hydroxypyrimidine (2·6 g.), thiourea (1·6 g.), hydrochloric acid (0·4 ml.), and water (100 ml.) were refluxed for 8 hr. After concentration to 30 ml. and refrigeration, the solid was recrystallised from water (*ca.* 100 ml.), giving the *sulphide* (0·2 g.), m. p. *ca.* 330° (decomp.) (Found: C, 43·35; H, 2·7; N, 24·9; S, 14·3. $C_8H_6N_4O_2S$ requires C, 43·25; H, 2·7; N, 25·2; S, 14·4%). The mother-liquors contained much of the starting material.

2,4-*Bismethylthiopyrimidine*.—2,4-Dimercaptopyrimidine (2·9 g.) in N-potassium hydroxide (37·5 ml.) was shaken for 1 hr. with methyl iodide (2·9 ml.). Chloroform-extraction (3 × 25 ml.) and distillation gave *bismethylthiopyrimidine*, b. p. 98°/0·25 mm., m. p. 9—10° (Found: C, 41·9; H, 4·9; N, 16·25. $C_6H_8N_2S_2$ requires C, 41·85; H, 4·7; N, 16·25%). Light absorption as neutral molecule at pH 7, $\lambda_{max.}$ 302, 252 (log ε 3·74, 4·27).

1,2,3,4-*Tetrahydro*-1,3-*dimethyl*-2,4-*dithiopyrimidine*.—1,3-Dimethyluracil (2 g.) and phosphorus pentasulphide (7·0 g.) in tetralin (45 ml.) were stirred at 180° for 4 hr. Volatile materials were removed at 130° *in vacuo*, and the pasty residue sublimed at 160°/0·05 mm. and recrystallised from water, to give the *dithiopyrimidine*, m. p. 121° (Found: C, 41·8; H, 4·6; N, 16·3. $C_6H_8N_2S_2$ requires C, 41·85; H, 4·7; N, 16·3%). Light absorption as neutral molecule at pH 5, $\lambda_{max.}$ 360 infl., 343, 286 (log ε 3·86, 3·98, 4·22).

Thiation in boiling pyridine gives 1,3-dimethyl-4-thiouracil in good yield, with m. p. 131—132° (depressed below 90° by admixture with the preceding compound) (Found: C, 46·3; H, 5·1; N, 17·8; S, 20·8. Calc. for $C_6H_8N_2OS$: C, 46·15; H, 5·15; N, 17·95; S, 20·5%). Light absorption as neutral molecule at pH 5, $\lambda_{max.}$ 328, 257 infl., 246 (log ε 4·30, 3·53, 3·56).

1-*Methyldithiouracil*.—1-Methyluracil was treated as above in tetralin. A solid separated when the reaction mixture cooled. This was extracted with hot 5N-ammonia (4 × 15 ml.), and the extract adjusted to pH 4·5. The precipitate was extracted with boiling water (5 × 250 ml.); refrigeration followed by sublimation at 150°/0·1 mm. gave 1-*methyldithiouracil* (0·6 g.), m. p. 255—260° (Found: C, 37·9; H, 3·9; N, 17·7. $C_5H_6N_2S_2$ requires C, 38·0; H, 3·8; N, 17·7%). Light absorption as neutral molecule at pH 5, $\lambda_{max.}$ 350, 276 (log ε 4·02, 4·34); as anion at pH 10, $\lambda_{max.}$ 313, 276, 219 (log ε 4·34, 4·26, 3·94).

We thank Professor A. Albert for helpful comment, and Messrs. D. Light, B. T. England, H. Satrapa, and F. Robinson for technical assistance.

Department of Medical Chemistry, Australian National University, Canberra, Australia. [*Received, October 6th*, 1960.]

[18] Brown, *J. Soc. Chem. Ind.*, 1950, **69**, 353.
[19] Wheeler and Johnson, *Amer. Chem. J.*, 1904, **31**, 591.
[20] Phillips, *J. Amer. Chem. Soc.*, 1951, **73**, 1061.

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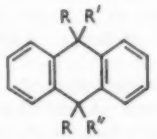
252. *Thiyl Radicals. Part I. Reactions of Anthracene with Oxygen and Thiols.*

By A. L. J. Beckwith and (Miss) Low * Beng See.

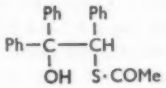
Anthracene reacts readily with thioacetic acid and oxygen, yielding 9,10-dihydro-9,10-di(acetylthio)anthracene and 9-(acetylthio)anthracene. Similar products are formed by reaction of anthracene and oxygen with thiobenzoic acid and with mercaptoacetic acid. With thiophenol and oxygen anthracene yields an unstable product formulated as a hydroperoxide, but the same reaction in the presence of acetic acid affords 9-phenylthioanthracene. Attempted reactions with toluene-ω-thiol and with dimercaptopropanol are described.

It is proposed that the reaction proceeds by free-radical chain addition, yielding a hydroperoxide which, in the presence of acids, is reduced to an alcohol and so converted into the final products by the usual ionic mechanism.

The reaction between anthracene, thioacetic acid, and oxygen was first described by Mikhailov and Blokhina [1] who observed that approximately one molar equivalent of the gas was rapidly absorbed and there were formed two isomeric 9,10-dihydro-9,10-di(acetylthio)anthracenes (I; R = H, R′ = R″ = Me·CO·S) and an unidentified yellow substance, m. p. 228—229°. 9,10-Dihydro-9,10-dimethyl-9,10-di(acetylthio)anthracene (I; R = Me, R′ = R″ = Me·CO·S) and 9,10-diethyl-9,10-dihydro-9,10-di(acetylthio)anthracene (I; R = Et, R′ = R″ = Me·CO·S) were produced from 9,10-dimethyl- and 9,10-diethylanthracene respectively by similar, though less rapid, reactions. In a later study [2] the



(I)



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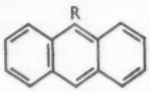

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same authors extended the reaction to 1,2-benzanthracene which yielded 9,10-dihydro-9,10-di(acetylthio)-1,2-benzanthracene, and to 9,9′-difluorenylidene and 9-benzylidenefluorene, both of which were converted into di(thiolacetates) by addition of CH_3·CO·S groups across the exocyclic double bonds. Products of somewhat different types were obtained from 1,1,2-triphenylethylene, which yielded *S*-(2-hydroxy-1,2,2-triphenylethyl) thioacetate (II), and from anthracene and thioacetic acid in ether, which produced 9,10-dihydro-9-acetylthioanthracene (I; R = R′ = H, R″ = Me·CO·S).

The structures of these products were not rigorously confirmed. The compounds obtained from anthracene were assigned the structure (I; R = H, R′ = R″ = Me·CO·S) on the basis of their oxidation to anthraquinone. No additional evidence was presented for the structures proposed for the products formed in reactions of substituted anthracenes.

The reaction mechanism originally put forward by Mikhailov and Blokhina [1] involved the addition across the reactive *meso*-positions of anthracene of two thioacetoxy-radicals formed by oxidation of thioacetic acid:

$$Me{\cdot}COSH + O_2 \longrightarrow Me{\cdot}COS{\cdot} + HO_2{\cdot}$$
$$Me{\cdot}COSH + HO_2{\cdot} \longrightarrow Me{\cdot}COS{\cdot} + H_2O_2$$

* Author's surname.

[1] Mikhailov and Blokhina, *Doklady Akad. Nauk S.S.S.R.*, 1951, **80**, 373.

[2] Mikhailov and Blokhina, *Problemy Mekhanizma Org. Reaktsii Akad. Nauk, Ukr. S.S.R.*; *Otdel. Fiz-Mat. i Khim. Nauk*, 1953, 215.

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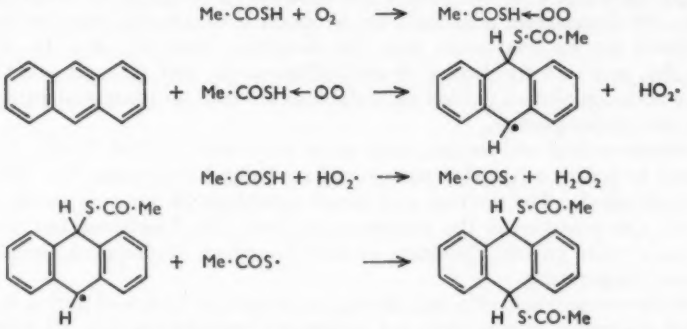
Later, the same authors,[2] aware that this mechanism accounts neither for the amount of oxygen absorbed nor for its rate of absorption, proposed a modified mechanism:



This mechanism is unsatisfactory: it does not account for the formation of 9,10-dihydro-9-(acetylthio)anthracene, and it involves an intermediate (Me·COS←OO) of a type never before described, for whose existence no direct evidence is offered.

These reactions show unusual features when compared with other free-radical reactions of anthracene. Thus, no bianthryl derivatives were isolated although attack of methyl,[3,4] benzyl,[4,5] 2-cyanopropyl,[6] phenyl,[4] and benzoylperoxy-radicals [7] on anthracene all lead to products of this type. Secondly, *meso*-disubstituted anthracenes, which usually do not readily undergo nuclear addition of free radicals,[8] reacted rapidly with thioacetic acid and oxygen. Finally, the thiol-catalysed dehydrogenation of 9,10-dihydroanthracene and its derivatives by azoisobutyronitrile [5,9] does not lead to products containing thio-groups although it involves the intermediate formation of free thiyl radicals.

With a view to resolve these inconsistencies we have now re-investigated the reaction of anthracene with thioacetic acid, and have extended it to other thiols. Similar reactions of substituted anthracenes have also been studied and will be described in Part II.

The main products from the reaction of anthracene with thioacetic acid and oxygen in benzene solution were the two isomeric 9,10-dihydro-9,10-di(acetylthio)anthracenes (I; R = H, R′ = R″ = Me·CO·S). These compounds, whose physical properties were similar to those described previously,[1] showed ultraviolet light absorption characteristic of substituted 9,10-dihydroanthracenes. The infrared spectra contained strong carbonyl bands, thus confirming the formation of a C–S bond between the aromatic nucleus and the mesomeric radical (Me·CO·S· ⟷ Me·CS·O·). Another major product was 9-(acetylthio)-anthracene (III; R = Me·CO·S), identified by comparison with a synthetic specimen. The close agreement between its properties and that of the reputed 9,10-dihydro-9-(acetylthio)anthracene [2] suggests that the two are identical: the analytical figures reported in the Russian work agree satisfactorily with those required by the fully aromatic compound. A fourth product, isolated in small yield, was di-(9-anthryl) disulphide; this appears to be identical with the unidentified yellow compound obtained by Mikhailov and Blokhina.[1]

When anthracene in benzene was treated under oxygen with other acidic compounds containing the SH group, similar reactions occurred. Thiobenzoic acid yielded both isomers of the addition product (I; R = H, R′ = R″ = Ph·CO·S), 9-(benzoylthio)-anthracene (III; R = Ph·CO·S), and a small amount of di-(9-anthryl) disulphide. The

[3] Beckwith and Waters, *J.*, 1956, 1108.
[4] Norman and Waters, *J.*, 1957, 950.
[5] Beckwith and Waters, *J.*, 1957, 1001.
[6] Bickel and Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.
[7] Turner and Waters, *J.*, 1956, 879.
[8] Beckwith, Norman, and Waters, *J.*, 1958, 171; Engelsma, Farenhorst, and Kooyman, *Rec. Trav. chim.*, 1954, **78**, 878.
[9] Bickel and Kooyman, *Nature*, 1952, **170**, 211.

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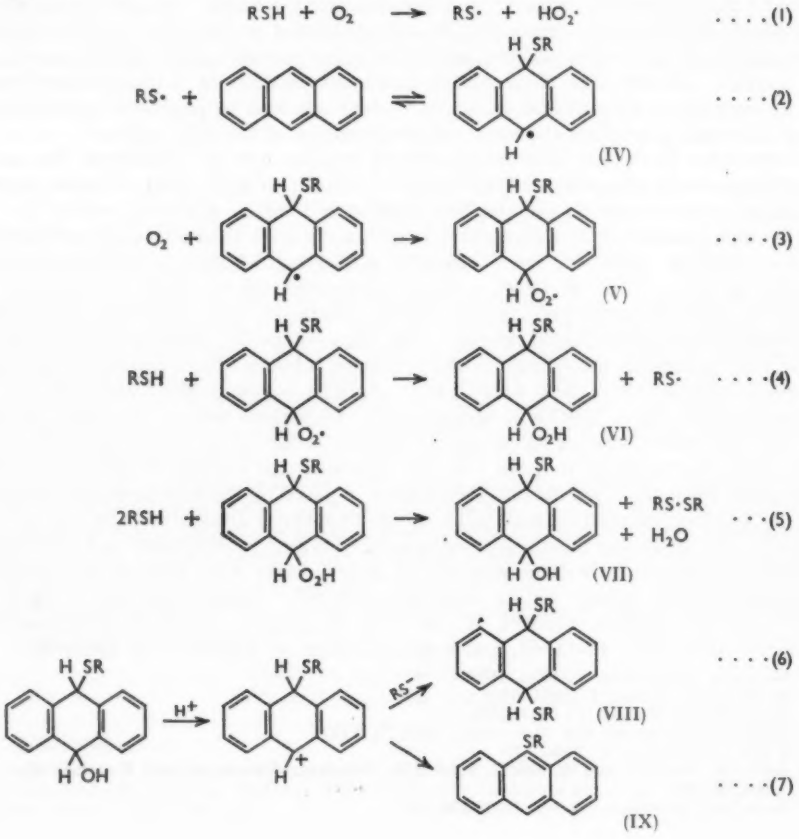
major product from reaction of anthracene in benzene with mercaptoacetic acid and oxygen was 9,10-di(carboxymethylthio)-9,10-dihydroanthracene (I; R = H, R′ = R″ = S·CH_2·CO_2H) of which only one isomer was isolated. Because of its instability and its insolubility, the dicarboxylic acid could not be obtained analytically pure, but its structure was confirmed by its conversion into the dimethyl ester (I; R = H, R′ = R″ = S·CH_2·CO_2Me), and into the known (9-anthrylthio)acetic acid (III; R = S·CH_2·CO_2H). The same reaction in alcohol yielded an unstable acid which on attempted purification was converted into anthraquinone.

With toluene-ω-thiol and oxygen, anthracene in benzene reacted slowly; the products were difficult to isolate and anthraquinone and unchanged anthracene were the only pure compounds obtained. The reaction with dimercaptopropanol was very similar. Anthraquinone was also produced in the analogous reaction with thiophenol, but the principal product was a white powder, insoluble in benzene, which decomposed vigorously when kept at room temperature.

In all of these experiments the rate of oxygen absorption decreased during the reaction. The oxygen-absorption curves were not accurately reproducible but all had a similar shape. In some cases there was an induction period of variable duration, but the absorption of oxygen could invariably be initiated by the addition of free-radical sources such as ferrous ion and cumene hydroperoxide.

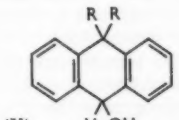
To account for these experimental observations we propose the following reaction mechanism:



The first steps (1—4), which are analogous to the reactions of olefins and of indene with thiols and oxygen,[10] account for the observation that the rate of oxygen absorption is proportional to the amount of anthracene present. It is suggested that with weakly acidic thiols the reaction proceeds no further and the products obtained are hydroperoxides (VI) or compounds resulting from their decomposition. We suggest that the unstable solid produced in the reaction of anthracene with thiophenol was the hydroperoxide (VI; R = Ph), and that the anthraquinone resulting from reactions with toluene-ω-thiol, with dimercaptopropanol, and with mercaptoacetic acid in alcohol was formed from similar hydroperoxides.

In the presence of acidic thiols the intermediate hydroperoxide is converted into addition and substitution products by the reactions (5—7). The feasibility of this mechanism has been demonstrated by treatment of cumene hydroperoxide with mercaptoacetic acid in benzene, (cumylthio)acetic acid being produced. Additional evidence was provided by reaction of 10,10-dibenzyl-9,10-dihydro-9-hydroxyanthracene (X; R = CH_2Ph) with mercaptoacetic acid, whereby the substituted acid (XI; R = CH_2Ph) was obtained. When 9,10-dihydro-9-hydroxyanthracene (X; R = H) was treated with mercaptoacetic acid, anthracene and 9-carboxymethylthio-9,10-dihydroanthracene (XI; R = H) were produced, thus providing analogies for the formation of both substitution (IX) and addition (VIII) products from intermediates of the type (VII). Finally, the reaction of anthracene with thiophenol and oxygen was repeated in the presence of acetic acid. As predicted by the above mechanism there was no unstable hydroperoxide formed and the only product isolated was 9-(phenylthio)anthracene.

The above mechanism is compatible with the formation of *S*-(2-hydroxy-1,2,2-triphenylethyl) thioacetate (II) from thioacetic acid and oxygen with 1,1,2-triphenylethylene as reported by Mikhailov and Blokhina.[2] It also accounts for some of the unusual features



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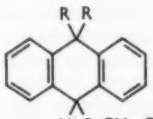

(XI)

of these reactions mentioned above. Thus, the absence of dimeric products may be attributed to the high concentration of oxygen, which acts as a scavenger for radicals of type (IV). By analogy with the mechanism for the free-radical addition of thiols to olefins [11] it is probable that reaction (2) is reversible. Under the more vigorous conditions employed for thiol-catalysed dehydrogenation of 9,10-dihydroanthracenes the equilibrium presumably favours the dissociation of (IV) to such an extent that formation of the addition product (VIII) cannot occur.

Reactions of thiols with aromatic compounds in the presence of oxygen may have biological significance. The premercapturic acids produced by metabolic oxidation of aromatic compounds [12] are known to have structures similar to, but of different orientation from, the intermediate (VII). Further, it is believed that metabolic hydroxylation of aromatic molecules involves reactions utilising a thiol and molecular oxygen, and is catalysed by ferrous ion.[13] Other reactions of polycyclic aromatic hydrocarbons with cell constituents containing the thiol group also appear possible. The above mechanism could account for the cross-linking of proteins, or for the irreversible binding of aromatic compounds to skin protein.[14] Interference with cell hydrogen-transfer processes by

[10] Oswald, *J. Org. Chem.*, 1959, **24**, 443; Ford, Pitkethly, and Young, *Tetrahedron*, 1958, **4**, 325.
[11] Walling and Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144.
[12] Boyland and Sims, *Biochem. J.*, 1958, **68**, 440; Knight and Young, *ibid.*, 1958, **70**, 111.
[13] Mitoma, Posner, Reitz, and Udenfriend, *Arch. Biochem. Biophys.*, 1956, **61**, 431; Mason, *Adv. Enzymology*, 1957, **19**, 177.
[14] Miller, *Cancer Res.*, 1951, **11**, 100; Bhargava, Hadler, and Heidelberger, *J. Amer. Chem. Soc.*, 1955, **77**, 2877; Bhargava and Heidelberger, *ibid.*, 1955, **78**, 3671.

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reactions of such thiols as glutathione or reduced thioctic acid with aromatic hydrocarbons may also occur.

Compounds required for reference or as starting materials were prepared by standard methods. 9,10-Dihydro-9-hydroxyanthracene (X; R = H) and 10,10-dibenzyl-9,10-dihydro-9-hydroxyanthracene (X; R = CH_2Ph) were produced by reduction of anthrone and 10,10-dibenzylanthrone respectively with lithium aluminium hydride, 9-(acetoxythio)-anthracene was prepared by reductive acetylation of di-(9-anthryl) disulphide, and (cumylthio)acetic acid resulted from the acid-catalysed addition of mercaptoacetic acid to α-methylstyrene.

Experimental

Ultraviolet absorption spectra were determined in ethanol, unless otherwise stated, on an Optica recording spectrophotometer. Adsorption chromatography was conducted on acid-washed alumina, hexane and hexane–benzene being used as eluants. Microanalyses were carried out by the C.S.I.R.O. and University of Melbourne Microanalytical Service.

Reaction of Anthracene with Thioacetic Acid.—A suspension of anthracene (5 g.) in thioacetic acid (20 ml.; b. p. 91—94°) and benzene (50 ml.) was shaken under oxygen at room temperature. Oxygen absorption was slow and became negligible after 7·5 hr. Unchanged anthracene (2·4 g.) was removed by filtration, and the solvent and excess of thioacetic acid were evaporated under a reduced pressure of nitrogen. When the residue was treated with methanol (50 ml.) a yellow solid was obtained, which on fractional crystallisation from methanol yielded anthracene (1 g.) and 9-(acetylthio)anthracene, m. p. and mixed m. p. 145—146°. The material obtained by evaporation of the mother-liquors when fractionally crystallised from hexane yielded sulphur (20 mg.), 9-(acetylthio)anthracene (total yield, 1·6 g.), and one isomer of 9,10-dihydro-9,10-di(acetylthio)anthracene (0·4 g.) which formed rods, m. p. 124·5—126° (Found: C, 66·1; H, 5·1; S, 19·9. Calc. for $C_{18}H_{16}O_2S_2$: C, 65·8; H, 4·9; S, 19·5%), $\lambda_{max.}$ 2547 Å (ε 10,810).

In a second experiment conducted under identical conditions there was a long induction period followed by rapid absorption of oxygen (550 ml.) during 2 hr. The crude product was isolated as before and separated into its constituents by chromatography on alumina. The products were 9-(acetylthio)anthracene, di-(9-anthryl) disulphide, m. p. 218—222°, and a second isomer of 9,10-dihydro-9,10-di(acetylthio)anthracene, which crystallised from hexane in rods, m. p. 145—147° (Found: C, 65·6; H, 5·0; S, 19·9%), $\lambda_{max.}$ 2360 Å (ε 17,080). All anthracene derivatives containing the acetylthio-group showed strong infrared carbonyl absorption at 1685—1695 $cm.^{-1}$.

Reaction of Anthracene with Thiobenzoic Acid.—When anthracene (18 g.) thiobenzoic acid (7 g.), and benzene (25 ml.) were shaken together under oxygen there was an initial rapid absorption of gas (*ca.* 90 ml. in 10 min.) but the reaction soon ceased and was then re-initiated by the addition of small amounts of cumene hydroperoxide and ferrous sulphate. After a total of 276 ml. of oxygen had been absorbed the mixture was washed with water and sodium carbonate solution and evaporated under a reduced pressure of nitrogen. Attempts to separate the residue into the pure components by crystallisation having failed, it was chromatographed on alumina. The following compounds were obtained: (i) anthracene (0·5 g.); (ii) di-(9-anthryl) disulphide (10 mg.); (iii) one *isomer* of 9,10-*dihydro*-9,10-*di*(*benzoylthio*)*anthracene* (0·5 g.), which crystallised from hexane–benzene in plates, m. p. 202—204° (Found: C, 74·5; H, 4·3; S, 13·9. $C_{28}H_{20}O_2S_2$ requires C, 74·3; H, 4·45; S, 14·2%), $\lambda_{max.}$ (in cyclohexane) 2390 (ε 37,000) and 2773 Å (ε 19,400); (iv) a second *isomer* (0·2 g.), which crystallised from hexane–benzene in prisms, m. p. 193·5—195·5°, mixed m. p. with the other isomer *ca.* 170° (Found: C, 74·6; H, 4·6; S, 13·7%), $\lambda_{max.}$ (in cyclohexane) 2390 (ε 31,410) and 2731 Å (ε 17,700); (v) 9-(*benzoylthio*)*anthracene* (0·2 g.), which crystallised from benzene–hexane in yellow prisms, m. p. 222—224° (Found: C, 80·1; H, 4·62; S, 10·1. $C_{21}H_{14}OS$ requires C, 80·2; H, 4·5; S, 10·2%), $\lambda_{max.}$ 3570 (ε 10,800), 3747 (ε 15,440), and 3950 Å (ε 13,380).

Reaction of Anthracene with Mercaptoacetic Acid.—(*a*) Anthracene (5 g.), mercaptoacetic acid (21 g.), and benzene (50 ml.) were shaken together under oxygen. When the initial rapid absorption of oxygen (660 ml. in 75 min.) had ceased, the mixture was extracted with aqueous sodium carbonate, and the extract was washed with ether and acidified with hydrochloric acid. The yellow precipitate was collected, washed, and treated with hot acetone. Crystallisation

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of the insoluble material from *NN*-dimethylformamide yielded plates (2·8 g.), m. p. 218—220°, of 9,10-*di*(*carboxymethylthio*)-9,10-*dihydroanthracene* (Found: C, 59·0; H, 4·7; S, 17·8. $C_{18}H_{16}O_4S_2$ requires C, 60·0; H, 4·5; S, 17·8%). The ultraviolet spectrum showed an inflexion at 2507 Å (ε 3660). The acetone-soluble material (2 g.) yielded a further quantity (1·8 g.) of the diacid on treatment with warm acetic acid. Esterification of the dicarboxylic acid with diazomethane yielded the *dimethyl ester*, which crystallised from ether in plates, m. p. 99—101·5° (Found: C, 61·7; H, 5·2; S, 16·6. $C_{20}H_{20}O_4S_2$ requires C, 61·8; H, 5·2; S, 16·5%).

When a suspension of the dicarboxylic acid (0·33 g.) in acetic acid (5 ml.) and hydrochloric acid (0·5 ml.) was heated a clear solution was rapidly obtained. Dilution with water yielded a precipitate of (9-anthrylthio)acetic acid (0·2 g.), which crystallised from ether–hexane in pale yellow needles, m. p. 166—167° (lit.,[15] m. p. 164°) (Found: C, 72·0; H, 4·7. Calc. for $C_{16}H_{12}O_2S$: C, 71·6; H, 4·5%), $\lambda_{max.}$ 2517 (ε 82,390), 3410 (ε 3040), 3557 (ε 4673), 3733 (ε 8519), and 3937 Å (ε 7560).

(*b*) A mixture of anthracene (0·9 g.), mercaptoacetic acid (5 ml.), and ethanol (20 ml.), when shaken under oxygen, absorbed gas very rapidly (total: 322 ml. in 1·6 hr.). Filtration then afforded anthraquinone (0·15 g.), and a further quantity (0·15 g.) of the same compound was obtained when the filtrate was evaporated and the residue treated with methanol. The methanol-soluble material was a red viscous liquid which dissolved readily in aqueous alkali. When it was reprecipitated with acid, however, it was converted in part into anthraquinone; no other product was isolated.

Reaction of Anthracene with Thiophenol.—(*a*) A mixture of anthracene (2·7 g.), thiophenol (10 ml.), and benzene was shaken under oxygen. Absorption of gas was initiated by the addition of small amounts of cumene hydroperoxide and ferrous sulphate, and was virtually complete after 7 hr. (total 340 ml.). A fine, white, insoluble powder (2 g.) which had slowly accumulated in the reaction mixture was filtered off and washed with benzene. When kept in air it rapidly became hot and decomposed to a dark brown resin (*A*). The filtrate was washed with aqueous sodium hydroxide to remove unchanged thiophenol, dried, and evaporated to 20 ml. under reduced pressure. After dilution with hexane the mixture was chromatographed on alumina. The first fraction was a mixture and was further resolved by repeated chromatography and fractional crystallisation. In this way there were obtained: (i) diphenyl disulphide (1·6 g.); (ii) a compound formulated as 9-(*phenylthio*)*anthracene*, which crystallised from hexane in yellow prisms (50 mg.), m. p. 100·5—102° (Found: C, 83·9; H, 4·9; S, 11·2. $C_{20}H_{14}S$ requires C, 83·9; H, 4·9; S, 11·2%), $\lambda_{max.}$ 2512 (ε 88,000), 2571 (ε 112,000), 3427 (ε 3726), 3585 (ε 5505), 3756 (ε 7551), and 3965 Å (ε 6850); (iii) yellow crystals (0·3 g.), m. p. 132·5—135° (Found: C, 86·6; H, 5·2; S, 8·5%), which could not be further purified (see next experiment.) Other fractions from the first chromatographic separation included anthraquinone (0·55 g.) and traces of highly coloured polar substances.

The decomposition product (*A*), when dissolved in hexane–benzene and chromatographed, yielded anthracene and anthraquinone as the only identifiable products.

A second experiment under identical conditions yielded the same insoluble product, which again rapidly decomposed although it was immediately transferred to a vacuum-desiccator.

(*b*) Anthracene (2·6 g.), thiophenol (10 ml.), acetic acid (10 ml.), and benzene (30 ml.) were shaken under oxygen. Absorption of oxygen (260 ml.) ceased after 6 hr. and the mixture was then filtered to remove unchanged anthracene (0·36 g.). The filtrate was washed with aqueous sodium hydroxide, dried, and evaporated under a reduced pressure of nitrogen. When the residue was treated with hot hexane (70 ml.) there remained an insoluble material (0·2 g.) which was separated into anthracene and anthraquinone. The hexane-soluble material was separated by chromatography on alumina into diphenyl disulphide (3·27 g.) and a yellow mixture (0·75 g.), m. p. *ca.* 125°. When the latter was heated under reduced pressure, diphenyl disulphide, anthracene, and a yellow substance, m. p. 130°, sublimed. The residue consisted of 9-(phenylthio)anthracene which crystallised from hexane in plates, m. p. 100·5—102°.

Reaction of Anthracene with Toluene-ω-thiol.—The thiol (10 ml.) was added to a suspension of anthracene (2·7 g.) and ferrous sulphate (50 mg.) in benzene (30 ml.), and the mixture shaken under oxygen. Absorption of gas was very slow (100 ml. in 11 hr.). The mixture was filtered from unchanged anthracene (1·3 g.). The filtrate was washed, dried, and evaporated under reduced pressure. When the residue was chromatographed on alumina the only identifiable compounds were anthracene (0·45 g.) and anthraquinone (90 mg.).

[15] Friedlander and Simon, *Ber.*, 1922, **55**, 3969.

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Reaction of Anthracene with 2,3-Dimercaptopropanol.—Addition of a small amount of ferrous sulphate initiated the absorption of oxygen by a mixture of anthracene (1·0 g.), 2,3-dimercaptopropanol (5 ml.), and benzene (30 ml.). After the absorption of 180 ml. of gas, the benzene solution was pale yellow, and a yellow, viscous precipitate had formed. When a drop of the benzene solution was chromatographed on acetylated paper three constituents were detected; two of these, anthracene (0·01 g.) and anthraquinone (0·1 g.) were separated by fractional crystallisation, but the third could not be isolated. The viscous precipitate, which resisted purification by crystallisation, was acetylated and chromatographed on alumina. The only identifiable fractions were anthracene (0·02 g.) and anthraquinone (0·05 g.).

Reaction of Cumene Hydroperoxide with Mercaptoacetic Acid.—A solution of cumene hydroperoxide (1·0 g.) and mercaptoacetic acid (3 ml.) in benzene (10 ml.) was stored under nitrogen for 2 weeks, then shaken with sodium carbonate solution, and the alkaline extract was washed with ether, acidified with hydrochloric acid, and set aside in the refrigerator. There was deposited (α,α-dimethylbenzylthio)acetic acid (0·72 g.), which recrystallised from hexane in needles, m. p. and mixed m. p. 69·5—70·5°.

When a similar mixture of reactants was shaken under oxygen for 5 days no absorption of gas was observed. Isolation of the product as above yielded only the same acid product (0·34 g.).

Reaction of 9,9-Dibenzyl-9,10-dihydro-10-hydroxyanthracene with Mercaptoacetic Acid.—The substituted hydroxyanthracene was prepared as follows: 10,10-Dibenzylanthrone (4 g.) and lithium aluminium hydride (0·15 g.) in ether (30 ml.) were refluxed for 1·8 hr. and the excess of anhydride was then destroyed by addition of ethyl acetate. When the mixture was shaken with dilute sulphuric acid, a precipitate of 9,9-dibenzyl-9,10-dihydro-10-hydroxyanthracene was formed, and a further quantity was obtained by evaporation of the ethereal solution. The hydroxy-compound crystallised from benzene in prisms (2·8 g., 70%), m. p. 174—177°.

When a solution of the foregoing hydroxy-compound (1·3 g.) and mercaptoacetic acid (5 ml.) in benzene (17 ml.) was kept under nitrogen for 3 days a crystalline precipitate (0·25 g.) of (*9,9-dibenzyl-9,10-dihydro-10-anthrylthio)acetic acid* was slowly formed. After filtration, the benzene solution was washed thrice with aqueous sodium carbonate, and the extract was acidified. The precipitated acid (0·63 g.) was collected, combined with that previously obtained, and crystallised from benzene, whence it formed needles, m. p. 208—210° (Found: C, 80·3; H, 5·9; S, 6·9. $C_{30}H_{26}O_2S$ requires C, 80·0; H, 5·8; S, 7·1%).

Reaction of 9,10-Dihydro-9-hydroxyanthracene with Mercaptoacetic Acid.—(*a*) A mixture of anthrone (2·0 g.), lithium aluminium hydride (0·2 g.), and ether (150 ml.) was stirred at room temperature for 1½ hr. and was then poured directly on to mercaptoacetic acid (10 ml.), kept overnight, and treated with dilute sulphuric acid. The aqueous portion was discarded, and the ethereal solution extracted with sodium carbonate solution. The alkaline extract was washed with ether and acidified. The precipitate of *9-carboxymethylthio-9,10-dihydroanthracene* (0·50 g.) crystallised from benzene–hexane in plates, m. p. 147—149° (Found: C, 71·0; H, 5·3; S, 12·4. $C_{16}H_{14}O_2S$ requires C, 71·1; H, 5·2; S, 11·9%), $\lambda_{max.}$ 2129 (ε 22,300), 2521 (ε 1525), 2660 (ε 1300), and 2751 Å (ε 1065). Evaporation of the ethereal solution yielded anthracene (0·32 g.).

(*b*) Anthrone (4 g.) was reduced with lithium aluminium hydride (0·4 g.) in ether (200 ml.). The mixture was treated with aqueous sodium hydroxide, and the ether layer was separated, washed, dried, and evaporated under a reduced pressure of nitrogen. The residue of 9,10-dihydro-9-hydroxyanthracene crystallised from light petroleum in fine needles (2·0 g.), m. p. 74° (lit.,[16] m. p. 76°). A solution of the foregoing hydroxy-compound (1·0 g.) and mercaptoacetic acid (10 ml.) in ether (25 ml.) was stored under nitrogen for 28 hr. Anthracene (80 mg.) was precipitated from the mixture and was collected. Extraction of the mixture with sodium carbonate solution yielded 9-carboxymethylthio-9,10-dihydroanthracene (0·22 g.). Anthracene (0·21 g.) was obtained by evaporation of the residual ethereal solution.

Preparation of Reference Compounds.—Di-(9-anthryl) disulphide. Anthracene was converted into 9-mercaptoanthracene *via* the dithio-chloride.[15] The crude thiol was dissolved in aqueous sodium hydroxide and oxidised to the disulphide with iodine. Di-(9-anthryl) disulphide crystallised from benzene in orange prisms, m. p. 218—222° (Found: C, 80·15; H, 4·4; S, 15·6. Calc. for $C_{28}H_{18}S_2$: C, 80·4; H, 4·3; S, 15·3%).

9-(Acetylthio)anthracene. Zinc dust (3·5 g.) was added in small portions to a warm mixture of di-(9-anthryl) disulphide (1·7 g.), sodium acetate (1 g.), and acetic anhydride (15 ml.). The

[16] von Perger, *J. prakt. Chem.*, 1881, **23**, 137.

mixture was boiled for 5 min., filtered whilst hot, and diluted with water. The precipitate of 9-(*acetylthio*)*anthracene* was collected, washed with water, and crystallised from hexane, forming yellow prisms (1·1 g., 54%), m. p. 146—147° (Found: C, 76·4; H, 4·9; S, 12·7. $C_{16}H_{12}OS$ requires C, 76·2; H, 4·8; S, 12·7%), $\lambda_{max.}$ 2487 (ε 82,680), 3557 (ε 5395), 3739 (ε 7597), and 3939 Å (ε 6200).

(*αα-Dimethylbenzylthio*)*acetic acid*. Concentrated sulphuric acid (5·0 ml.) was added dropwise with stirring to α-methylstyrene (5·0 g.) and mercaptoacetic acid (10 ml.) in acetic acid (25 ml.). After the addition the warm solution was set aside for 2 hr., then diluted with water, and extracted with ether. The ethereal solution was washed with water and extracted with aqueous potassium hydroxide. The oily precipitate of the required acid, which was formed on acidification of the alkaline extract, solidified on cooling. It crystallised from hexane in rods (7·2 g., 80%), m. p. 70—71° (Found: C, 63·1; H, 6·8; S, 15·5. Calc. for $C_{11}H_{14}O_2S$: C, 62·9; H, 6·7; S, 15·2%).

We thank Mr. A. G. Moritz for measuring infrared absorption spectra. One of us (L. B. S.) gratefully acknowledges the receipt of a Fellowship from the Commonwealth Government of Australia under the Colombo Plan.

THE UNIVERSITY, ADELAIDE, S. AUSTRALIA. [*Received, June 7th*, 1960.]

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253. *Acetylenic Compounds Related to Stilbœstrol. Part III.*[1,2] *Acetylenic Alcohols derived from α-Alkyldeoxyanisoins, and the α-Alkyl-β-ethynylstilbenes.*

By C. W. SHOPPEE, J. CYMERMAN CRAIG, and RUTH E. LACK.

Deoxyanisoin, and its α-methyl and α-ethyl analogues, condense with ethynylmagnesium bromide to give the expected acetylenic alcohols in good yield. The product obtained from α-ethyldeoxyanisoin is the diastereoisomer of that reported as formed on use of sodium acetylide in dioxan.

Dehydration of the acetylenic alcohol (I; R = R′ = H) from deoxyanisoin by either acetic anhydride or phosphorus trichloride in pyridine gave the *trans*-stilbene (II; R = H) in good yield. The α-methyl analogue (I; R = Me, R′ = H) with phosphorus tribromide in chloroform gave by cyclisation the indene (V), accompanied by a Meyer–Schuster rearrangement to the αβ-unsaturated ketone (VII; R = Me). This ketone was also obtained when phosphorus trichloride in pyridine was used, together with the chloroallene (XIII; R = Me), but attempted dehydration by methanolic sulphuric acid yielded the methyl ether (I; R = R′ = Me) and the αβ-unsaturated aldehyde (VIII; R = Me) formed by a Rupe rearrangement.

The α-ethyl analogue (I; R = Et, R′ = H) with phosphorus trichloride in pyridine afforded the αβ-unsaturated ketone (VII; R = Et) (Meyer–Schuster reaction) and the chloro-allene (XIII; R = Et), which was dehydrohalogenated by sodamide in liquid ammonia to the *trans*-stilbene (II; R = Et). The stilbene was also obtained as an amorphous hydrate, believed from spectroscopic evidence to be the *cis*-isomer.

The acetylenic diol (I; R = OH, R′ = H) with phosphorus trichloride in pyridine gave an indene (XX) by cyclisation and rearrangement of an intermediate dichloro-allene, and also the 1,3-diketone (XXI), formed by ketonisation of the dienol resulting from a Meyer–Schuster reaction. The mechanism of the latter rearrangement is discussed.

ALTHOUGH deoxyanisoin condenses normally with hex-1-yne and propyne *via* the Grignard reagent,[1] reaction with sodium or lithium acetylide in liquid ammonia results in molecular fission to give *p*-anisic acid, *p*-anisamide, and 1-*p*-methoxyphenylprop-2-ynol. Similar

[1] Cymerman Craig, Martin, Moyle, and Wailes, *Austral. J. Chem.*, 1956, **9**, 373, is regarded as Part I of this series.

[2] Cymerman Craig, Moyle, Rowe-Smith, and Wailes, *Austral. J. Chem.*, 1956, **9**, 391, is regarded as Part II of this series.

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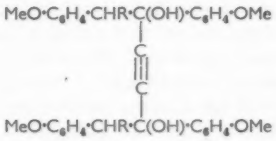
fission had earlier been found [2] on attempted condensation of benzil or benzoin with the same reagent. The desired acetylenic alcohol (I; R = R′ = H) has, however, been isolated in low yield after prolonged reaction of the ketone with acetylenedimagnesium bromide at 20°. Attempts to increase the yield by carrying out the reaction under reflux gave a product identified by synthesis as 2-methoxy-6-*p*-methoxyphenylnaphthalene.[1]

(I) MeO·C$_6$H$_4$·CHR·C(OR′)(C≡CH)·C$_6$H$_4$·OMe

(II) MeO·C$_6$H$_4$·CR=C(C≡CH)·C$_6$H$_4$·OMe



(III)

Condensation of deoxyanisoin [3] with ethynylmagnesium bromide [4] gave an excellent yield of a product which, after separation from a trace of the dienyne, 1,2,5,6-tetra-*p*-methoxyphenylhexa-1,5-dien-3-yne,[1] was treated with Girard reagent P to remove unchanged ketone. Chromatography of the non-ketonic fraction yielded approximately equal amounts of the acetylenic ether (I; R = H, R′ = Et), formed by etherification of the parent alcohol during the Girard separation, the vinylacetylene (II; R = H) and the alcohol (I; R = R′ = H), identical with the material previously obtained.[1] The vinylacetylene (II; R = H) had the spectral properties of a *trans*-stilbene, and in ethanolic solution was isomerised to the *cis*-compound by ultraviolet light. When heated, it readily dimerised, as shown by a molecular-weight determination (Rast); a normal value for the monomer was obtained by the cryoscopic technique.

When the reaction was carried out for a shorter period and the mixture was worked up by means of methanol, without treatment with Girard's reagent, chromatography afforded the corresponding methyl ether (I; R = H, R′ = Me), unchanged deoxyanisoin, and the alcohol (I; R = R′ = H). Some of the diol (III; R = H) was also obtained. The ethers (I; R = H, R′ = Et and Me respectively) were identical with samples prepared from the parent alcohol with ethanol and methanol, respectively, by acid-catalysis.

When α-methyldeoxyanisoin was prepared by the method of Dodds, Golberg, Lawson, and Robinson,[5] the product had m. p. 43°; these authors reported a value of 53—57° for their material. The two crystalline modifications (we are indebted to Dr. R. I. Cox for the sample, m. p. 53°) showed essentially identical infrared spectra. Reaction of this ketone with ethynylmagnesium bromide gave a small amount of the diol (III; R = Me) and an excellent yield of the alcohol (I; R = Me, R′ = H).

α-Ethyldeoxyanisoin had the m. p. reported by Wilds and Biggerstaff,[6] and condensed readily with ethynylmagnesium bromide to yield a trace of the diol (III; R = Et) and, as the main product, the amorphous alcohol (I; R = Et, R′ = H), which gave correct analytical figures and eventually crystallised as a hydrate, m. p. 43°, shown from its infrared spectrum to be intramolecularly hydrogen-bonded. When this preparation was repeated under heat-wave conditions of unusually low humidity (<15%) and high temperature (39—42°), this alcohol was obtained as a solid, m. p. 105°, showing ultraviolet absorption identical with that of the hydrate.

Hofstetter and Wilder Smith [7] reported the preparation of the alcohol (I; R = Et, R′ = H) as a solid, m. p. 95°, by interaction of the ketone with sodium acetylide in dioxan. The ultraviolet absorption spectrum of their compound (for which we are indebted to Dr. E. Hofstetter) was substantially identical with that of our material, m. p. 105°, but a mixed m. p. showed a depression to 80—83°.

These isomers were shown to be the two possible diastereoisomeric racemates by

[3] Carter, Cymerman Craig, Lack, and Moyle, *J.*, 1959, 476.
[4] Jones, Skatteböl, and Whiting, *J.*, 1956, 4765.
[5] Dodds, Golberg, Lawson, and Robinson, *Proc. Roy. Soc.*, 1939, *B*, **127**, 140.
[6] Wilds and Biggerstaff, *J. Amer. Chem. Soc.*, 1945, **67**, 789.
[7] Hofstetter and Wilder Smith, *Helv. Chim. Acta*, 1953, **36**, 1706.

catalytic hydrogenation: for the hydrate of m. p. 43° afforded 3,4-di-*p*-methoxyphenylhexan-3-ol, m. p. 83°, while Hofstetter and Wilder Smith's [7] compound of m. p. 95° gave the isomeric saturated alcohol, m. p. 115°. Both forms of this hexanol have been obtained by Wilds and Biggerstaff [6] from α-ethyldeoxyanisoin with ethylmagnesium bromide. It is interesting that the reaction of this ketone with ethynylmagnesium bromide should lead entirely to the diastereoisomer of m. p. 105°, while reaction with sodium acetylide in dioxan [7] gave rise to an oil from which only the material of m. p. 95° could be obtained crystalline. That this oil consisted of a mixture of the two possible racemates was shown by its catalytic hydrogenation [7] to a mixture of the stereoisomeric di-*p*-methoxyphenylhexanols, identical with that obtained by Dodds, Golberg, Lawson, and Robinson.[5] The reason for this is undoubtedly to be sought in the steric inhibition to attack of the bulky ethynylmagnesium bromide–tetrahydrofuran complex on the ketone group of α-ethyldeoxyanisoin, itself strongly enveloped by the hindering α-ethyl group, and thus spatially equivalent to a phenyl t-butyl ketone, known to be sterically retarded towards normal Grignard addition.

Anisoin readily reacted with an excess of ethynylmagnesium bromide, to give the diol (I; R = OH, R′ = H), together with some of the tetrol (III; R = OH).

The ultraviolet absorption spectra of the alcohols of types (I) and (III) exhibited, as expected, $\lambda_{max.}$ 230 mμ (ε *ca.* 20,000) and 275 mμ (ε *ca.* 3000), characteristic of the 4-methoxybenzyl alcohol chromophore, as in 1,2-di-*p*-methoxyphenylethanol.[2]

The alcohol (I; R = R′ = H) was unaffected by treatment with potassium hydrogen sulphate in toluene at 130°, whilst the use of the same reagent at 210° for 30 seconds gave only an insoluble polymer. Acetic anhydride at 100° for 2 hr. was ineffective, but at 130° after 0·75 hr. the vinylacetylene (II; R = H) was obtained in 50% yield. By doubling the reaction time this yield was raised to 65%, but 20% of polymer and 20% of unchanged alcohol were also obtained; increase of the reaction period to 3 hr. reduced the yield of stilbene to 33% and increased that of polymer to 40%, no alcohol being recovered. The ease of polymerisation of the product indicated the need for a low-temperature dehydration method, and use of phosphorus trichloride in pyridine at 20° readily gave an excellent yield of the stilbene (II; R = H), which showed light absorption ($\lambda_{max.}$ 219 and 329 mμ) identical with that of the related *trans*-stilbenes previously reported.[1] On irradiation it was transformed into the *cis*-isomer ($\lambda_{max.}$ 221 and 308 mμ) with reduced intensity of the longer-wavelength band; similar *trans* ⟶ *cis* changes have been previously noted[1] for stilbene derivatives.[2,8,9]

The alcohol (I; R = Me, R′ = H) was unchanged by acetic anhydride at 140° for 2 hr., but treatment with phosphorus tribromide in chloroform at 0° produced two substances. The first product, m. p. 85°, had the composition and molecular weight of the stilbene (II; R = Me) but was yellow and had an infrared spectrum devoid of absorption in both of the regions associated with the C≡CH and C=C groupings. Earlier work [1] on the alcohol (I; R = R′ = H) gave an unexpected cyclisation product, 2-methoxy-6-*p*-methoxyphenylnaphthalene (IV; R = R′ = H), but analogous formulation of the compound, m. p. 85°, as (IV; R = Me, R′ = H) was excluded by the absence of the three ultraviolet absorption peaks characteristic of a 2-phenylnaphthalene.[1] The compound showed intense absorption at 905 cm.$^{-1}$ characteristic of the vinylidene group, and this, together with its colour, indicated cyclisation in the alternative way to give 6-methoxy-2-*p*-methoxyphenyl-3-methyl-1-methyleneindene (V); on recrystallisation and heating to 70°, the material was transformed into a high-melting colourless substance of unchanged composition, no longer absorbing in the vinylidene region. A similar cyclisation has been reported by Hofstetter and Wilder Smith,[10] who found that the related vinyl alcohol (VI) with dehydrating agents gave 3-ethyl-6-methoxy-2-*p*-methoxyphenyl-1-methylindene.

[8] Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948—1949, *A*, **241**, 147.
[9] Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1940, **62**, 2973.
[10] Hofstetter and Wilder Smith, *Helv. Chim. Acta*, 1953, **36**, 1949.

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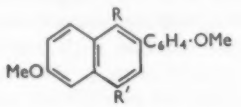
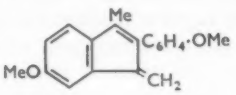
The second product was the αβ-unsaturated ketone (VII; R = Me), identified by its infrared absorption at 1650 cm.$^{-1}$ and its 2,4-dinitrophenylhydrazone, and derived from the alcohol (I; R = Me, R′ = H) by a Meyer–Schuster rearrangement.[11]

(IV) 



(V)

$MeO{\cdot}C_6H_4{\cdot}CHEt{\cdot}C(OH)(CH{=}CH_2){\cdot}C_6H_4{\cdot}OMe$ (VI)

$MeO{\cdot}C_6H_4{\cdot}CR{=}C(COMe){\cdot}C_6H_4{\cdot}OMe$ (VII)

On treatment with methanolic sulphuric acid at 70°, the alcohol (I; R = Me, R′ = H), gave the methyl ether (I; R = R′ = Me), exhibiting light absorption identical with the ether (I; R = H, R′ = Me) and with the alcohols (I; R′ = H). A second product, isomeric with the ketone (VII; R = Me), was the αβ-unsaturated aldehyde (VIII; R = Me), formed from the alcohol (I; R = Me, R′ = H) by the Rupe rearrangement;[12] its analogue (VIII; R = Et) was obtained by Hofstetter and Wilder Smith[10] from the alcohol (I; R = Et, R′ = H). The mechanism of this rearrangement has been postulated[13] to be anionotropic change of the system (IX; X = OH) *via* the allenic carbonium ion (X) to the allenic enol (XI; X = OH), which tautomerises to give the αβ-unsaturated aldehyde (XII).

(VIII) $MeO{\cdot}C_6H_4{\cdot}CHR{\cdot}C(=CH{\cdot}CHO){\cdot}C_6H_4{\cdot}OMe$

(IX) $X{\cdot}CRR'{\cdot}C{\equiv}CH$ $\quad CRR'{=}C{=}CH^+$ (X)

(XI) $CRR'{=}C{=}CHX$ $\quad CRR'{=}CH{\cdot}CHO$ (XII)

(XIII) $MeO{\cdot}C_6H_4{\cdot}CHR{\cdot}C(=C{=}CHCl){\cdot}C_6H_4{\cdot}OMe$

With phosphorus trichloride in pyridine at 20° the alcohol (I; R = Me, R′ = H) gave the chloro-allene (XIII; R = Me), showing intense absorption at 1920 cm.$^{-1}$ characteristic of the allene group, in agreement with the known lowering of the frequency of the allenic absorption band from its normal position (1950 cm.$^{-1}$) to 1900—1930 cm.$^{-1}$ when conjugated.[14,15] The formation of the chloro-allene (XIII; R = Me) provides a further example of the ready rearrangement of the system (IX; X = Cl or OH) to the allene (XI; X = Cl);[16] and similar allenic halides have recently been isolated.[17] The αβ-unsaturated aldehyde (VIII; R = Me) was not found, but a second product was the αβ-unsaturated ketone (VII; R = Me), previously obtained from the alcohol (I; R = Me, R′ = H) by use of phosphorus tribromide and formed by a Meyer–Schuster rearrangement.

This reaction[11] had been earlier postulated to proceed by a dehydration-hydration mechanism,[18] but this suggestion is made untenable by Newman's demonstration[19] that conversion of the system (XIV) into (XVII) may be carried out at room temperature in the presence of sulphonated polystyrene (Dowex 50) as source of hydrogen ions, in conditions under which neither hydration of the triple bond nor dehydration of tertiary alcohols occurred.

[11] Meyer and Schuster, *Ber.*, 1922, **55**, 819.
[12] Rupe, *Helv. Chim. Acta*, 1926, **9**, 672; 1928, **11**, 449, 656, 965; 1931, **14**, 708.
[13] MacGregor, *J. Amer. Chem. Soc.*, 1948, **70**, 3953.
[14] Celmer and Solomons, *J. Amer. Chem. Soc.*, 1953, **75**, 1372.
[15] Oroshnik, Mebane, and Karmas, *J. Amer. Chem. Soc.*, 1953, **75**, 1050.
[16] Favorski and Favorskaya, *Compt. rend.*, 1935, **200**, 839; Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 386, 1237; 1942, **12**, 638; 1948, **18**, 52; Favorskaya and Favorskaya, *ibid.*, 1940, **10**, 451; Favorskaya and Zakharova, *ibid.*, 1940, **10**, 446; Nagibina, *ibid.*, 1940, **10**, 427; Hennion, Sheehan, and Maloney, *J. Amer. Chem. Soc.*, 1950, **72**, 3542; Hennion and Maloney, *ibid.*, 1951, **73**, 4735.
[17] Ford, Thompson, and Marvel, *J. Amer. Chem. Soc.*, 1935, **57**, 2619; Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 461; Jacobs and Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314; Jacobs, Teach, and Weiss, *ibid.*, 1955, **77**, 6254.
[18] Hennion, Davis, and Maloney, *J. Amer. Chem. Soc.*, 1949, **71**, 2813.
[19] Newman, *J. Amer. Chem. Soc.*, 1953, **75**, 4740.

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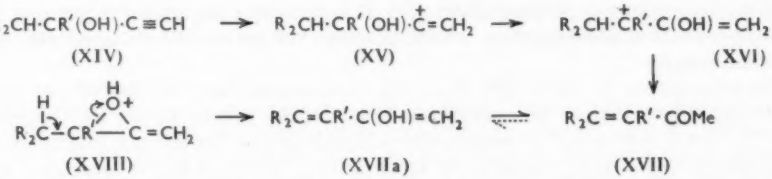
Newman [19] proposed a mechanism involving a 1,2-hydroxyl shift in an initially formed conjugate acid (XV) to the enolic carbonium ion (XVI), which eliminates a proton from the adjacent carbon atom and ketonises to yield the product (XVII). Such 1,2-hydroxyl shifts are, however, unknown, and we prefer to formulate this step as occurring through an intermediate epoxide oxonium salt (XVIII), readily formed by nucleophilic attack of the hydroxyl group in (XV) on the adjacent carbonium carbon atom; the oxide undergoes ring-fission with simultaneous loss of a proton directly to furnish the enolic form (XVIIa) of (XVII).



The alcohol (I; R = Et, R′ = H) was unchanged in refluxing acetic anhydride for 2 hr., but with phosphorus trichloride in pyridine at 0° gave the chloro-allene (XIII; R = Et), showing infrared absorption at 1920 cm.$^{-1}$, and the αβ-unsaturated ketone (VII; R = Et), previously obtained by Hofstetter and Wilder Smith [10] on attempted dehydration of the alcohol (I; R = Et, R′ = H) under acidic conditions (the 2,4-dinitrophenylhydrazones were identical).

When the chloro-allene (XIII; R = Et) was treated with a suspension of sodamide in liquid ammonia which still contained unchanged sodium, dehydrohalogenation was accompanied by reduction to give the known *meso*- and racemic isomers [20] of 3,4-di-*p*-methoxyphenylhexane, and the partially reduced 3,4-di-*p*-methoxyphenylhex-1-yne, showing light absorption in agreement with this structure. From its m. p. range the latter is probably a mixture of the two possible diastereoisomeric racemates.

Repetition of the experiment with precautions to ensure the absence of unconverted sodium gave an excellent yield of the stilbene (II; R = Et), m. p. 125°, $\lambda_{max.}$ 223 mμ (ε 14,600) and 284 mμ (ε 12,200). The slight bathochromic shift of the former, and the very marked hypsochromic shift and reduced intensity of the latter, maximum, compared with those of the compound (II; R = H), are characteristic of αβ-dialkyl-substituted stilbenes,[8,21] in which steric repulsions largely destroy the coplanarity of the chromophoric system.

After having been kept in sunlight for several weeks, a dilute ethanolic solution of the compound (II; R = Et) showed $\lambda_{max.}$ 226, 242, and 277 mμ (ε 21,300, 24,700, and 9900 respectively). The displacement of the long- and short-wavelength maxima are in agreement with the known *trans* ⟶ *cis* conversion.[1,8,9] The new maximum at 242 mμ, however, is reminiscent of the peak (247 mμ) reported by Buckles [22] to result from the irradiation of dilute ethanolic solutions of *cis*- and *trans*-stilbene and ascribed by him to the formation of phenanthrene, which was isolated and identified. Similar absorption maxima in the 250 mμ region were observed for *cis*-stilbene derivatives by Braude.[21] Such a cyclisation may occur, in the sterically favourable *cis*-isomer, by a photochemical reaction resulting in the loss of two hydrogen atoms to produce a diradical which stabilises itself by bond formation between the two adjacent aromatic rings.

The stilbene (II; R = Et) was also obtained as an amorphous hydrate, m. p. 90—92°, showing infrared absorption characteristic of a hydrogen-bonded hydroxyl group. When the chloro-allene was prepared from Hofstetter and Wilder Smith's isomer,[7] m. p. 95°,

[20] Buu-Hoï, Ng, and Hoán, *J. Org. Chem.*, 1949, **14**, 1023; Schmelkes, U.S.P. 2,385,472/1945; *Chem. Abs.*, 1946, **40**, 176.

[21] Braude, *J.*, 1949, 1902; Oki, *Bull. Chem. Soc. Japan*, 1953, **26**, 37, 161, 331; Grundy, *Chem. Rev.*, 1957, **57**, 281; Miquel, *Tetrahedron*, 1960, **8**, 205.

[22] Buckles, *J. Amer. Chem. Soc.*, 1955, **77**, 1040.

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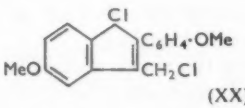
of the alcohol (I; R = Et, R′ = H) (for which we are indebted to Dr. E. Hofstetter) and treated with sodamide in liquid ammonia, the same hydrate, m. p. 90—93°, was obtained. Its ultraviolet absorption ($\lambda_{max.}$ 228, 275 mμ; ε = 21,000 and 8000) was essentially that of the irradiation product of the *trans*-stilbene (II; R = Et), m. p. 125°; the hydrate, m. p. 90—92°, is therefore regarded as the *cis*-isomer of this stilbene. It is clear that if the formation of the stilbene proceeds *via* the intermediate chloro-allene (XIII; R = Et), then both diastereoisomeric racemates of the alcohol (I; R = Et, R′ = H) are capable of furnishing the same form of the dehydration product (II; R = Et), as observed. Catalytic hydrogenation of the stilbene (II; R = Et) gave the known mixture of isomers of 3,4-di-*p*-methoxyphenylhexane, identical with that previously obtained and with an authentic sample.

The ethynyldiol (I; R = OH, R′ = H) from anisoin was unchanged on prolonged treatment with an excess of methylmagnesium iodide, known to act as a dehydrating agent.[23] It was converted by phosphorus trichloride in pyridine into a colourless substance possessing no hydroxylic, acetylenic, or ketonic function in its infrared spectrum; analysis showed this to contain two chlorine atoms, and it is presumably a cyclisation product of the intermediate dichloro-allene (XIX). Its ultraviolet spectrum ($\lambda_{max.}$ 254, 322 mμ; ε = 12,500 and 26,000) does not agree with the naphthalene structure (IV; R = R′ = Cl)

(XIX) $MeO\cdot C_6H_4\cdot CHCl\cdot C(=C=CHCl)\cdot C_6H_4\cdot OMe$

(XXI) $MeO\cdot C_6H_4\cdot CO\cdot CH(COMe)\cdot C_6H_4\cdot OMe$

(XXII) $MeO\cdot C_6H_4\cdot C(OH)=C[C(OH)=CH_2]\cdot C_6H_4\cdot OMe$



(XX)

which would show absorption resembling that of its parent compound (IV; R = R′ = H) with the expected bathochromic shift due to the halogen. The long-wavelength maximum indicates a conjugated system resembling that of a *trans*-stilbene, and from its stability and lack of colour it may be the indene derivative (XX), produced by migration into conjugation of the exocyclic double-bond first formed on cyclisation of the dichloro-allene (XIX). Similar indene derivatives, exhibiting ready migration of the central ethylenic linkage,[10] have been obtained from dienœstrol [24] and shown to have light absorption resembling that of *trans*-stilbene.[25] The observed bathochromic shift of the low-wavelength maximum in (XX) may be due to hyperconjugation by the two allylic chlorine atoms. A second product was the β-diketone (XXI), $\nu_{max.}$ 1720 (CO) and 1650 cm.$^{-1}$ (C=C–C=O), previously obtained [2] by reaction of α-bromodeoxyanisoin with sodium acetylide in ammonia, giving a bis-2,4-dinitrophenylhydrazone and with hydroxylamine yielding deoxyanisoin oxime; the diketone arises by Meyer–Schuster rearrangement of the diol (I; R = OH, R′ = H), and subsequent ketonisation of the dienol (XXII).

Experimental

Ultraviolet absorption spectra were determined for 95% EtOH solutions on a Hilger " Unispek " instrument; infrared spectra were measured on a Perkin–Elmer " Infracord " spectrophotometer, and m. p.s on a Kofler block.

1,2-*Di*-p-*methoxyphenylbut*-3-*yn*-2-*ol* (I; R = R′ = H).—(*a*) A solution of ethylmagnesium bromide, prepared from magnesium (4·8 g.) in tetrahydrofuran (140 c.c.), was added in 1 hr. to a saturated solution of acetylene in tetrahydrofuran (80 c.c.) at 0° (Jones, Skatteböl, and

[23] Jacquemain, *Compt. rend.*, 1934, **198**, 483; Brachin, *Bull. Soc. chim. France*, 1906, **35**, 1177; Wilson and Hyslop, *J.*, 1923, 2612.

[24] Lane and Spialter, *J. Amer. Chem. Soc.*, 1951, **73**, 4408; Hausmann and Wilder Smith, *Nature*, 1948, **161**, 892; *J.*, 1949, 1030.

[25] Solmssen, *J. Amer. Chem. Soc.*, 1943, **65**, 2370.

Whiting [4]). Deoxyanisoin [3] (25·6 g.) was added and the mixture was heated under reflux for 18 hr. After addition of saturated ammonium chloride solution and acidification with sulphuric acid, the product was extracted into ether. On evaporation of the solvent, 1,2,5,6-tetra-*p*-methoxyphenylhexa-1,5-dien-3-yne separated as yellow prisms, m. p. 226° (1·63 g.), mixed m. p. with authentic sample [1] 226°. To remove unchanged deoxyanisoin the residual red oil was treated with Girard P reagent (24 g.) in absolute alcohol (240 c.c.) and acetic acid (24 g.) for 1 hr. at 100°, poured on ice (2·5 l.) containing potassium carbonate (24·84 g.), and extracted into benzene. The resulting oil was adsorbed from hexane on to aluminium oxide (500 g.). Elution with hexane (5 × 500 c.c.) gave 3-*ethoxy*-3,4-*di*-p-*methoxyphenylbut*-1-*yne* (I; R = H, R′ = Et) (9·76 g.), m. p. 70° [Found (after drying at 20°/0·5 mm. for 5 hr.): C, 77·6; H, 7·3; O, 15·7; active H, 0·3%; *M*, 310. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·15; O, 15·5; 1 active H, 0·3%; *M*, 289], $\nu_{max.}$ 3260 (C≡CH), 2115 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 19,500 and 3300 respectively).

Further elution with 1 : 4 benzene–hexane (8 × 500 c.c.) gave 1,2-*di*-p-*methoxyphenylbut*-1-*en*-3-*yne* (II; R = H), m. p. 85° (from hexane) (7·8 g.) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 81·6; H, 6·2; O, 12·2; active H, 0·37%; *M* (Rast), 567; *M* (depression of f. p. of benzene) 262. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; O, 12·1; 1 active H, 0·37%; *M*, 264], $\nu_{max.}$ 3240 (C≡CH), 2080 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 219, 329 mμ (ε 19,500 and 28,800 respectively). After the solution had been in the sun for several hr. it had $\lambda_{max.}$ 221, 308 mμ (ε 25,700 and 20,800 respectively).

Elution with ether (3 × 500 c.c.) gave 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (I; R = R′ = H) (7·64 g.), m. p. 95° (from benzene–hexane) (lit.,[1] 95°) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·5; H, 6·4; O, 16·7; active H, 0·68%; *M* (Rast), 267. Calc. for $C_{18}H_{18}O_3$: C, 76·55; H, 6·4; O, 17·0; 2 active H, 0·71%; *M*, 282], $\nu_{max.}$ 3440 (OH), 3230 (C≡CH), 2115 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 20,450 and 3225 respectively).

(*b*) A second experiment carried out by refluxing the Grignard reactants for 6 hr., decomposing the complex with ammonium chloride, acidifying the mixture with sulphuric acid, and extracting it with ether gave a red oil. This was dissolved in a little methanol, leaving a white insoluble material, m. p. 180—184°. Recrystallisation from acetone gave 1,2,5,6-*tetra*-p-*methoxyphenylhex*-3-*yne*-2,5-*diol* (III; R = H), m. p. 194—195° (5·63 g.) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 75·7; H, 6·3; active H, 0·37; OMe, 22·0. $C_{34}H_{34}O_6$ requires C, 75·8; H, 6·35; 2 active H, 0·37; OMe, 23·2%], $\nu_{max.}$ 3480 (OH), 2050 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 228, 275 mμ (ε = 18,100 and 3030 respectively). After removal of the methanol, the residual oil was adsorbed on a column of aluminium oxide (500 g.). Elution with pentane (200 c.c.) gave 3-*methoxy*-3,4-*di*-p-*methoxyphenylbut*-1-*yne* (I; R = H, R′ = Me) (3·0 g.), m. p. 62° (from pentane) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·8; H, 6·6; O, 16·1; OMe, 28·7; active H, 0·27. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8; O, 16·2; OMe, 31·2; 1 active H, 0·3%], $\nu_{max.}$ 3230 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 19,800 and 2780 respectively). Further elution with 1 : 4 hexane–benzene gave deoxyanisoin (10·5 g.), m. p. and mixed m. p. 111°. Elution with ether gave 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (I; R = R′ = H) (2·4 g.), m. p. 95° undepressed with the sample prepared as in (*a*) above.

3-*Ethoxy*-3,4-*di*-p-*methoxyphenylbut*-1-*yne* (I; R = H, R′ = Et).—1,2-Di-*p*-methoxyphenylbut-3-yn-2-ol (I; R = R′ = H) (500 mg.) and ethanol (10 c.c.) were treated with conc. sulphuric acid (2 drops) for 1 hr. at 80°. After neutralisation of the acid and evaporation the residual oil was adsorbed from hexane on aluminium oxide (10 g.). Elution with pentane gave 3-ethoxy-3,4-di-*p*-methoxyphenylbut-3-yne (I; R = H, R′ = Et) (120 mg.), m. p. and mixed m. p. 68—69°.

3-Methoxy-3,4-di-*p*-methoxyphenylbut-1-yne, similarly prepared by reaction in methanol at 65°, had m. p. and mixed m. p. 59—61°.

α-*Methyldeoxyanisoin*.—α-Methyldeoxyanisoin was prepared in 68·5% yield by the method of Dodds, Golberg, Lawson, and Robinson,[5] from deoxyanisoin (25·6 g.), methyl iodide (14·2 g.), and sodium (2·3 g.) in alcohol (50 c.c.), followed by further sodium (2·3 g.) in alcohol (50 c.c.). It formed prisms (from hexane), m. p. 43° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 75·3; H, 6·7. Calc. for $C_{17}H_{16}O_3$: C, 75·5; H, 6·7%]. The infrared spectrum for this material was essentially identical with that of a sample of m. p. 52—53°, kindly provided by Dr. R. I. Cox. Dodds *et al.*[5] report m. p. 53—57°.

3,4-*Di*-p-*methoxyphenylpent*-1-*yn*-3-*ol* (I; R = Me, R′ = H).—A solution of ethylmagnesium bromide (from magnesium, 2·43 g.) in dry tetrahydrofuran (60 c.c.) was added in 1 hr. to a

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saturated solution of acetylene in tetrahydrofuran (50 c.c.) at 0°. α-Methyldeoxyanisoin (13·6 g.) was then added and the mixture was refluxed for 18 hr. The Grignard complex was extracted with ether, decomposed with ammonium chloride, acidified with sulphuric acid, and washed with sodium hydrogen carbonate solution. On partial evaporation of the solvent a white solid, m. p. 204—209°, separated; recrystallisation from acetone gave **2,3,6,7-*tetra*-p-*methoxyphenyloct*-4-*yne*-3,6-*diol*** (III; R = Me) (2·68 g.), m. p. 217° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·15; H, 6·8; O, 17·1; active H, 0·4%; *M* (Rast), 656. $C_{36}H_{38}O_6$ requires C, 76·30; H, 6·8; O, 16·95; 2 active H, 0·35%; *M*, 567], $\nu_{max.}$ 3500 (OH), 2040 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 18,300 and 3120 respectively). Complete removal of the solvent from the filtrate gave a yellow solid which was adsorbed on aluminium oxide (200 g.) from hexane. Elution with benzene (3 × 250 c.c.) and ether (4 × 250 c.c.) gave **3,4-*di*-p-*methoxyphenylpent*-1-*yn*-3-*ol*** (I; R = Me, R′ = H), m. p. 112—113° (from benzene–hexane) (9·74 g.) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 77·0; H, 6·8; O, 15·9; active H, 0·65%; *M* (Rast), 283. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8; O, 16·2; 2 active H, 0·67%; *M*, 296], $\nu_{max.}$ 3470 (OH), 3220 (C≡H), 2105 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 21,950, 3020 respectively).

α-Ethyldeoxyanisoin.—Interaction of deoxyanisoin (90 g.), ethyl iodide (54·8 g.), sodium 8·1 g.), and alcohol (150 c.c.) by the method of Dodds, Golberg, Lawson, and Robinson [5] gave, on cooling, unchanged deoxyanisoin (47·0 g.), m. p. and mixed m. p. 111°. The filtrate was extracted with ether and the resulting oil was adsorbed on aluminium oxide (1 kg.). Elution with hexane (6 × 500 c.c.) gave α-ethyldeoxyanisoin (48 g.), m. p. 47—48°, previously given by Wilds and Biggerstaff,[6] although Dodds, Golberg, Lawson, and Robinson [5] reported it as an oil [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 75·9; H, 7·05. Calc. for $C_{18}H_{20}O_3$: C, 76·05; H, 7·0%].

3,4-*Di*-p-*methoxyphenylhex*-1-*yn*-3-*ol* (I; R = Et, R′ = H).—(*a*) A solution of ethylmagnesium bromide (from magnesium, 3·66 g.) in dry tetrahydrofuran (150 c.c.) was added in 1 hr. to a saturated solution of acetylene in tetrahydrofuran (80 c.c.) at 0°. α-Ethyldeoxyanisoin (21·3 g.) was added and the mixture heated under reflux for 18 hr. Working up as above gave an oil that was adsorbed on aluminium oxide (600 g.). Successive elution with hexane (6 × 250 c.c.), 1 : 4 benzene–hexane (250 c.c.), and benzene (3 × 200 c.c.) gave amorphous **3,4-*di*-p-*methoxyphenylhex*-1-*yn*-3-*ol*** (I; R = Et, R′ = H) (16·4 g.) [Found (after drying at 50°/0·5 mm. for 24 hr.): C, 77·3; H, 7·2; O, 15·6; active H, 0·62. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·1; O, 15·5; 2 active H, 0·65%], $\nu_{max.}$ 3460, 3530 (OH), 3230, 3275 (C≡CH), 2110 (C≡C) cm.$^{-1}$. This crystallised from hexane as a *hydrate*, m. p. 43° [Found (after drying at 20°/760 mm. for 48 hr.): C, 73·3; H, 7·32; active H, 0·89%; *M*, 265. $C_{20}H_{22}O_3,H_2O$ requires C, 73·2; H, 7·35; 2 active H, 0·89%; *M*, 328], $\nu_{max.}$ 3535, 3460 (OH), 3225 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 20,700 and 3020 respectively). The infrared spectrum (OH bands) was unaffected by the concentrations of carbon tetrachloride solutions, indicating the hydrate to be intramolecularly bonded. Further elution with ether (3 × 500 c.c.) gave **3,4,7,8-*tetra*-p-*methoxyphenyldec*-5-*yne*-4,7-*diol*** (III; R = Et), m. p. 204—205° (from acetone) [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·4; H, 7·0; O, 16·1; active H, 0·37%; *M*, 558. $C_{38}H_{42}O_6$ requires C, 76·7; H, 7·1; O, 16·1; 2 active H, 0·34%; *M*, 594], $\nu_{max.}$ 3570 (OH) 2060 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 229, 275 mμ, (ε 22,200 and 3420 respectively).

(*b*) A second preparation on the same scale was carried out when the laboratory temperature was 39—42° with ~15% humidity. After isolation in the usual manner the product was adsorbed on aluminium oxide (600 g.). Elution with hexane (8 × 200 c.c.) gave unchanged α-ethyldeoxyanisoin (7·55 g.), m. p. 45—46°. Further elution with benzene and ether gave **3,4-*di*-p-*methoxyphenylhex*-1-*yn*-3-*ol*** (I; R = Et, R′ = H), m. p. 105° (12·5 g.) [Found (after drying at 80°/0·5 mm. for 72 hr.): C, 77·1; H, 7·2; O, 16·0; active H, 0·65. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·14; O, 15·5; 2 active H, 0·65%], $\nu_{max.}$ 3500 (OH) 3275 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε = 19,500, 3250 respectively).

Hydrogenation of **3,4-*Di*-p-*methoxyphenylhex*-3-*yn*-2-*ol*.**—(*a*) A solution of 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol hydrate (200 mg.) in methanol (10 c.c.) was shaken with pre-reduced platinum oxide (40 mg.) in methanol (10 c.c.) under hydrogen (absorption, 27 c.c.). Filtration and evaporation gave 3,4-di-*p*-methoxyphenylhexan-3-ol, m. p. 83° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·4; H, 8·0. Calc. for $C_{20}H_{26}O_3$: C, 76·4; H, 8·3%], $\nu_{max.}$ 3570 (OH) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 19,000 and 3100 respectively).

(*b*) A solution of 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol, m. p. 95° (100 mg.) (prepared by Hofstetter and Wilder Smith [7]), in methanol (10 c.c.) was added to a suspension of pre-reduced

platinum and hydrogenated as above (absorption, 13 c.c.). It gave 3,4-di-*p*-methoxyphenylhexan-3-ol, m. p. 115° [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 76·5; H, 8·0%], $\nu_{max.}$ 3570 (OH) cm.$^{-1}$, $\lambda_{max.}$ 230, 275 mμ (ε 18,900 and 3100 respectively). The infrared absorption curves of these two diastereoisomers were almost identical. Wilds and Biggerstaff [6] isolated both isomers (*a*), m. p. 83—85° and (*b*), m. p. 114—117° after treating α-ethyldeoxyanisoin with ethylmagnesium bromide in ether.

1,2-*Di*-p-*methoxyphenylbut*-3-*yne*-1,2-*diol* (I; R = OH, R′ = H).—Ethylmagnesium bromide (from magnesium, 3·63 g.) in tetrahydrofuran (140 c.c.) was added in 1 hr. to a saturated solution of acetylene in tetrahydrofuran (80 c.c.) at 0°. Anisoin (13·6 g.) was added and the mixture was heated under reflux for 18 hr. After the usual working up, a white solid separated from the ether solution. Recrystallisation from acetone gave 1,2,5,6-*tetra*-p-*methoxyphenylhex*-3-*yne*-1,2,5,6-*tetraol* (III; R = OH), m. p. 217° (4·95 g.) [Found (after drying at 20°/5 mm. for 12 hr.): C, 71·43; H, 6·0; O, 22·1; active H, 0·69. $C_{34}H_{34}O_8$ requires C, 71·55; H, 6·0; O, 22·4; 2 active H, 0·7%], $\nu_{max.}$ 3390 (OH), 2060 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 237, 274, 280 mμ (ε 19,000, 2975, and 2550 respectively). Evaporation of the ether gave a brown oil which was adsorbed on aluminium oxide (300 g.). Elution with benzene–hexane (1 : 1; 4 × 150 c.c.) gave unchanged anisoin, m. p. and mixed m. p. 111° (5·3 g.). Further elution with benzene (2 × 75 c.c.) and ether (100 c.c.) gave 1,2-*di*-p-*methoxyphenylbut*-3-*yne*-1,2-*diol* (I; R = OH, R′ = H), m. p. 107° [Found (after drying at 20°/0·5 mm. for 8 hr.): C, 72·4; H, 6·15; O, 21·2; active H, 1·0. $C_{18}H_{18}O_4$ requires C, 72·45; H, 6·1; O, 21·45; 3 active H, 1·0%], $\nu_{max.}$ 3495, 3590 (OH), 3260 (C≡CH), 2110 (C≡C) cm.$^{-1}$, $\lambda_{max.}$ 234, 274, 280 mμ (ε 19,000, 3000, 2680 respectively).

1,2-*Di*-p-*methoxyphenylbut*-1-*en*-3-*yne* (II; R = H).—(*a*) Phosphorus trichloride (1·5 c.c.) was added to 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (500 mg.) in dry pyridine (10 c.c.) at 0°. After 15 hr. at 20° the mixture was added dropwise to ice and water (50 c.c.). Ether-extraction afforded an oil which was adsorbed from hexane on aluminium oxide (15 g.). Successive elution with hexane (2 × 50 c.c.), hexane–benzene (1 : 1; 2 × 100 c.c.), and benzene (100 c.c.) gave 1,2-di-*p*-methoxyphenylbut-1-en-3-yne (415 mg.), m. p. 82—84° (from hexane). The infrared absorption curve was identical with, and the m. p. did not depress that of, an authentic sample.

(*b*) Treatment of 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (200 mg.) with acetic anhydride (10 c.c.) at 130° for 0·75 hr. gave a yellow oil after ether-extraction; adsorption from hexane on to aluminium oxide (10 g.) and elution with hexane (100 c.c.) gave 1,2-di-*p*-methoxybut-1-en-3-yne, m. p. and mixed m. p. 85° (100 mg.).

(*c*) Treatment of 1,2-di-*p*-methoxyphenylbut-3-yn-2-ol (1·1 g.) with acetic anhydride (30 c.c.) at 130° for 1·5 hr. under nitrogen gave a brown oil after ether-extraction. This was adsorbed from hexane on aluminium oxide (30 g.). Elution with hexane (3 × 50 c.c.) gave 1,2-di-*p*-methoxyphenylbut-1-en-3-yne (684 mg.), m. p. and mixed m. p. 84°. Further elution with benzene (2 × 50 c.c.) gave a dark polymer (220 mg.); elution with ether (3 × 50 c.c.) afforded unchanged alcohol, m. p. 94° (231 mg.).

(*d*) When experiment (*c*) was repeated with a reaction time of 3 hr., the yield of stilbene was 370 mg., whilst that of the polymer increased to 455 mg. No unchanged alcohol was isolated.

Attempted Preparation of 2,3-*Di*-p-*methoxyphenylpent*-2-*en*-4-*yne* (II; R = Me).—(*a*) 3,4-Di-*p*-methoxyphenylpent-1-yn-3-ol (8·0 g.) in chloroform (10 c.c.) was treated with phosphorus tribromide (8 g.) in chloroform (10 c.c.) at 0°. After 4 hr. at 20° the mixture was cooled to 0° and poured into ice-cold ethanol, diluted with water, and extracted with ether. Evaporation of the dried ether extracts at 20° gave a yellow oil which was adsorbed from pentane on aluminium oxide (250 g.). Elution with pentane gave 6-*methoxy*-2-p-*methoxyphenyl*-3-*methyl*-1-*methyleneindene* (V) (3·87 g.), m. p. 85°, as yellow needles from methanol [Found (after drying at 20°/1 mm. for 24 hr.): C, 81·3; H, 6·6; OMe, 21·5%; *M* (f. p. in benzene), 242. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5; OMe, 22·3%; *M*, 278], $\lambda_{max.}$ 221, 267 mμ (ε 23,000 and 37,300 respectively), no further absorption up to 350 mμ. The infrared absorption curve showed an absence of bands in the OH, C=O, C≡CH and C≡C regions but included $\nu_{max.}$ 905 cm.$^{-1}$ (C=CH_2). This compound would not form a 2,4-dinitrophenylhydrazone, gave a negative test with Tollens's reagent, and showed a negative iodoform reaction. Recrystallisation from methanol gave a white insoluble *substance*, m. p. 141°. After drying at 40°/0·5 mm. for 12 hr., the m. p. had increased to 245° (Found: C, 81·0; H, 6·7. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%), and the infrared absorption curve had no band in the region corresponding to OH, C=O, C≡CH, C≡C, and C=CH_2.

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Further elution with benzene (3 × 150 c.c.) gave an αβ-unsaturated ketone, $\nu_{max.}$ 1650 cm.$^{-1}$ (2·5 g.), which gave the 2,4-*dinitrophenylhydrazone*, m. p. 75°, of 3,4-di-*p*-methoxyphenylpent-3-en-2-one (VII; R = Me) [Found (after drying at 20°/0·5 mm. for 24 hr.): C, 62·6; H, 5·15. $C_{25}H_{24}O_6N_4$ requires C, 63·0; H, 5·1%].

(*b*) 3,4-Di-*p*-methoxyphenylpent-1-yn-3-ol (1 g.) in dry methanol (10 c.c.) was treated with 20% sulphuric acid (2 c.c.) for 0·25 hr. at 70°. The acid was neutralised with sodium hydrogen carbonate and the product extracted into ether. The resulting oil was adsorbed from pentane on aluminium oxide (30 g.). Elution with pentane (4 × 20 c.c.) gave 3-*methoxy*-3,4-*di*-p-*methoxyphenylpent*-1-*yne* (I; R = R′ = Me) (200 mg.) as a colourless oil [Found (after drying at 20°/0·5 mm. for 24 hr.): C, 77·1; H, 7·35. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·15%], $\nu_{max.}$ 3200s (C≡CH), 2115w cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 230, 275 mμ (ε 20,400 and 3450 respectively). Further elution with benzene–hexane (1 : 20; 20 c.c.) and (1 : 10; 2 × 20 c.c.) afforded a yellow oil (735 mg.), $\nu_{max.}$ 1670s cm.$^{-1}$ (C=C–C=O). This gave a positive test with Schiff's reagent, showed a negative iodoform reaction, and readily formed the 2,4-*dinitrophenylhydrazone*, m. p. 185°, of 3,4-di-*p*-methoxyphenylpent-2-enal (VIII; R = Me) as red needles from ethanol–ethyl acetate [Found (after drying at 60°/0·5 mm. for 8 hr.): C, 62·8; H, 5·0. $C_{25}H_{24}N_4O_6$ requires C, 63·0; H, 5·1%].

(*c*) Phosphorus trichloride (1·5 c.c.) in pyridine (10 c.c.) was added to 3,4-di-*p*-methoxyphenylpent-1-yn-3-ol (500 mg.) in pyridine (10 c.c.) at 0°. After 3 hr. at 20°, the mixture was added dropwise to ice and water (50 c.c.), extracted with ether, and washed with dilute sulphuric acid and sodium hydrogen carbonate solution. Evaporation afforded an oil which was adsorbed from pentane on aluminium oxide (15 g.). Elution with pentane (3 × 20 c.c.) yielded 1-chloro-3,4-di-*p*-methoxyphenylpenta-1,2-diene (XIII; R = Me) as a colourless oil (250 mg.) giving a positive Beilstein test, $\nu_{max.}$ 1920s, 1890w cm.$^{-1}$ (C=C=C), $\lambda_{max.}$ 224, 278 mμ (ε 18,100 and 14,900 respectively). Further elution with benzene (3 × 50 c.c.) gave a yellow oil (120 mg.) containing a mixture of the chloro-allene and an αβ-unsaturated carbonyl compound, $\nu_{max.}$ 1920m, 1890w, 1650m cm.$^{-1}$. This oil formed the 2,4-dinitrophenylhydrazone, m. p. 75°, of 3,4-di-*p*-methoxyphenylpent-3-en-2-one (VII; R = Me) which did not depress the m. p. of the sample described in (*a*).

3,4-*Di*-p-*methoxyphenylhex*-3-*en*-1-*yne* (II; R = Et).—(*a*) Phosphorus trichloride (30 c.c.) in pyridine (20 c.c.) was added dropwise to 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol (m. p. 105°) (10 g.) in pyridine (200 c.c.) at −40°. After 4 hr. at 0° the mixture was poured slowly on ice and water (1 l.). Ether-extraction afforded a product which was adsorbed from pentane on neutral aluminium oxide (300 g.). Elution with pentane (8 × 50 c.c.) and pentane–ether (1 : 20; 5 × 50 c.c.) gave 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (XIII; R = Et) (5·92 g.), $\nu_{max.}$ 1920s, 1890s cm.$^{-1}$ (C=C=C), n_D^{25} 1·607, which was not further purified before use in the following experiment. Further elution with ether (6 × 50 c.c.) gave an oil (3·2 g.) consisting of a mixture of the chloro-allene and an αβ-unsaturated carbonyl compound, $\nu_{max.}$ 1920m, 1890w, 1650m cm.$^{-1}$, that formed the 2,4-dinitrophenylhydrazone, m. p. 80—82°, of 3,4-di-*p*-methoxyphenylhex-3-en-2-one [Found (after drying at 20°/0·5 mm. for 24 hr.): C, 63·5; H, 5·4. Calc. for $C_{26}H_{26}N_4O_6$: C, 63·7; H, 5·35%]. This sample did not depress the m. p. of a sample, m. p. 75—80°, obtained from Hofstetter and Wilder Smith.[10]

(*b*) Finely powdered ferric nitrate (50 mg.) and sodium (0·25 g.) were added to a stirred solution of ammonia (200 c.c.) at −35°. Further sodium (3 g.) was added in small pieces followed after 0·5 hr. by 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (4·0 g.) in dry ether (10 c.c.). After the mixture had been stirred at −35° for 1 hr., ether (50 c.c.) and ammonium chloride)3 g.) were added. Evaporation of the ammonia and extraction into ether gave a yellow product which was adsorbed from hexane on aluminium oxide (100 g.). Elution with hexane (5 × 30 c.c.) and benzene–hexane (1 : 20, 2 × 30 c.c.) gave 3,4-di-*p*-methoxyphenylhexane (3·1 g.), m. p. 133—145° [Found (after drying at 60°/0·5 mm. for 4 hr.): C, 80·35; H, 8·6. Calc. for $C_{20}H_{26}O_2$: C, 80·5; H, 8·8%], $\lambda_{max.}$ 230, 275 mμ (ε 21,400 and 3530 respectively). The infrared spectrum showed no band in the OH, C≡CH, C≡C, and C=O regions. Two isomers are reported [20] to have m. p. 133° and 144°. Further elution with ether–hexane (1 : 20; 30 c.c.) gave an oil which crystallised from methanol to give 3,4-*di*-p-*methoxyphenylhex*-1-*yne*, m. p. 25—30° [Found (after drying at 20°/0·5 mm. for 4 hr.): C, 81·3; H, 8·0. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·6%], $\nu_{max.}$ 3240m (C≡CH), 2080w cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 228, 278 mμ (ε 19,550 and 3420).

(*c*) To stirred ammonia (500 c.c.) at −35° was added ferric nitrate (100 mg.) and sodium

(1·5 g.) in small pieces. No blue colour of dissolved sodium remained after 0·5 hr. but the mixture was stirred for a further 1·5 hr., then 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (1·5 g.) in ether (25 c.c.) was added dropwise at −40°. After 0·5 hr. the usual working up gave an oil, $\nu_{max.}$ 3240m (C≡CH) and 2080w cm.$^{-1}$ (C≡C), which was adsorbed from pentane on aluminium oxide (40 g.). The product was not eluted with pentane or benzene but ether–benzene (1 : 20; 7 × 25 c.c.) gave a yellow oil (1·04 g.), $\nu_{max.}$ 3240m (C≡CH), 2080w cm.$^{-1}$ (C≡C). Rechromatography gave 3,4-*di*-p-*methoxyphenylhex*-3-*en*-1-*yne* (II; R = Et) (400 mg.), m. p. 125°, as needles from methanol [Found (after drying at 20°/0·5 mm. for 3 hr.): C, 81·75; H, 6·9. $C_{20}H_{20}O_2$ requires C, 82·15; H, 6·9%], $\nu_{max.}$ 3240m (C≡CH), 2080w cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 223, 284 mμ (ε 14,600 and 12,200 respectively). After 4 weeks in sunlight this absorption had changed to $\lambda_{max.}$ 226, 242, 277 mμ (ε 21,320, 24,760, and 9900 respectively). The oily fractions of the stilbene gradually crystallised and had m. p. 125° after several days.

(*d*) In a preliminary experiment, 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (500 mg.) was added to sodamide prepared from sodium (1 g.) and ammonia (100 c.c.) as described in (*c*). Ether-extraction gave a reddish-brown oil, giving a negative Beilstein test, which was absorbed from pentane on aluminium oxide (10 g.). Elution with pentane and benzene gave only oils (130 mg.), $\nu_{max.}$ 3250w (C≡CH) and 1650m cm.$^{-1}$ (C=C–C=O); further elution, with ether–benzene (1 : 5; 2 × 20 c.c.), gave a yellow oil (300 mg.), $\nu_{max.}$ 3250s (C≡CH), 2115w cm.$^{-1}$ (C≡C). Addition of pentane to its solution in ether precipitated cis-3,4-*di*-p-*methoxyphenylhex*-3-*en*-1-*yne hydrate*, m. p. 90—92° as a yellow amorphous solid [Found (after drying at 20°/0·5 mm. for 2 hr.): C, 77·3; H, 6·95. $C_{20}H_{20}O_2,H_2O$ requires C, 77·4; H, 7·15%], $\nu_{max.}$ 3400m (OH), 3240m (C≡CH), 2080vw cm.$^{-1}$ (C≡C), $\lambda_{max.}$ 228, 275 mμ (ε 20,800 and 8000 respectively). A mixed m. p. with the alcohol,[7] m. p. 95—97° (for which we are indebted to Dr. E. Hofstetter), was depressed to 70—75°.

(*e*) Repetition of the above experiment but with 1-chloro-3,4-di-*p*-methoxyphenylhexa-1,2-diene (500 mg.) prepared from 3,4-di-*p*-methoxyphenylhex-1-yn-3-ol, m. p. 95—97° (Hofstetter and Wilder Smith [7]), gave an identical product, m. p. 90—93°.

Hydrogenation of 3,4-*Di*-p-*methoxyphenylhex*-1-*en*-3-*yne*.—3,4-Di-*p*-methoxyphenylhex-1-en-3-yne (70 mg.), m. p. 125°, in ethyl acetate (20 c.c.) with pre-reduced Adams catalyst (15 mg.) absorbed 18 c.c. of hydrogen at 25°/760 mm. in 40 min. Complete hydrogenation of the stilbene to 3,4-di-*p*-methoxyphenylhexane requires 17·5 c.c. Filtration and evaporation gave a yellow oil which was absorbed from pentane on aluminium oxide (2 g.). Elution with pentane (2 × 25 c.c.) gave 3,4-di-*p*-methoxyphenylhexane (51 mg.), m. p. 133—144°, which did not depress the melting point of an authentic sample.[39]

Attempted Dehydration of 1,2-*Di*-p-*methoxyphenylbut*-3-*yne*-1,2-*diol*.—(*a*) Phosphorus trichloride (2·0 c.c.) was added to 1,2-di-*p*-methoxyphenylbut-3-yne-1,2-diol (500 mg.) in dry pyridine (10 c.c.) at 0°. After 3 hr. at 20° the mixture was added dropwise to ice and water (50 c.c.). Ether-extraction afforded a colourless material crystallising from ethanol to give 1-*chloro*-3-*chloromethyl*-5-*methoxy*-2-p-*methoxyphenylindene* (XX), m. p. 114° (210 mg.) [Found (after drying at 20°/0·5 mm. for 4 hr.): C, 64·75; H, 5·05. $C_{18}H_{16}Cl_2O_2$ requires C, 64·5; H, 4·8%], $\lambda_{max.}$ 254, 322 mμ (ε 12,480 and 26,000 respectively) with end-absorption at 210 mμ (ε 18,000). The infrared spectrum showed no band in the OH, C≡CH, C≡C, and C=O regions. The mother-liquors were evaporated and the resulting oil was adsorbed from pentane on aluminium oxide (10 g.). Elution with pentane (2 × 20 c.c.) gave a further quantity of the indene, m. p. 114° (50 mg.). Further elution with benzene–pentane (1 : 5; 2 × 20 c.c.) and benzene (2 × 20 c.c.) gave an oil (150 mg.), $\nu_{max.}$ 1720 (C=O) and 1650 cm.$^{-1}$ (C=C–C=O), affording the hydrated *bis*-2,4-*dinitrophenylhydrazone* of 1,2-di-*p*-methoxyphenylbutane-1,3-dione as needles (from ethanol), m. p. 254° [Found (after drying at 20°/0·5 mm. for 12 hr.): C, 53·1; H, 4·6. $C_{30}H_{26}O_{10}N_8,H_2O$ requires C, 53·25; H, 4·2%]. Treatment of the oil with hydroxylamine hydrochloride and sodium hydroxide for 1 hr. gave deoxyanisoin oxime, m. p. 120—121° [Found (after drying at 20°/0·5 mm. for 8 hr.): C, 71·0; H, 6·35. Calc. for $C_{16}H_{17}NO_3$: C, 70·8; H, 6·3%]. A mixed m. p. with an authentic specimen [2] was undepressed.

We are grateful to Dr. E. Hofstetter for helpful information and samples for mixed m. p. determinations; we thank Dr. R. I. Cox for a specimen of α-ethyldeoxyanisoin, m. p. 53°, and Miss B. Stevenson for the microanalyses.

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[*Received, July 29th,* 1960.]

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254. *The Microwave Spectrum, Structure, and Nuclear Quadrupole Coupling Coefficients of Nitrosyl Chloride.*

By D. J. Millen and J. Pannell.

Nitrosyl chloride enriched in ^{18}O has been prepared and, from its microwave spectrum, rotational constants have been evaluated. These have been combined with those of the ^{35}Cl and ^{37}Cl isotopic species of normal nitrosyl chloride to yield the molecular dimensions: $r_{N-Cl} = 1{\cdot}975$ Å, $r_{N-O} = 1{\cdot}139$ Å, and $\angle ONCl = 113° 20'$. From the hyperfine structure of the spectra, chlorine nuclear quadrupole coupling parameters, $eQ.\partial^2V/\partial a^2 = -48{\cdot}7$, $eQ.\partial^2V/\partial b^2 = 29{\cdot}4$, and $eQ.\partial^2V/\partial c^2 = 19{\cdot}3$ Mc./sec. were obtained for $N^{16}O^{35}Cl$, and $eQ.\partial^2V/\partial a^2 = -38{\cdot}4$, $eQ.\partial^2V/\partial b^2 = 23{\cdot}2$, and $eQ.\partial^2V/\partial c^2 = 15{\cdot}2$ Mc./sec. for $N^{16}O^{37}Cl$. The coupling parameters have been interpreted in terms of bond properties, and comparison made with nitryl chloride. It is concluded that the nitrogen–chlorine bond is not only appreciably more ionic (in the sense NO^+Cl^-) but also has more double-bond character than the corresponding bond in nitryl chloride.

An apparatus is described for the preparation of ^{18}O-enriched oxygen by electrolysis of about 0·6 ml. quantities of water, leaving a residue of only 0·1 ml.

The rotational constants of two isotopic species of a triatomic molecule provide in principle sufficient information to determine the molecular dimensions completely. In the case of nitrosyl chloride, however, the two species $NO^{35}Cl$ and $NO^{37}Cl$ which are readily examined in natural abundance do not permit a unique structure to be pin-pointed with useful precision; pairs of N–Cl and N–O distances over an appreciable range are compatible with the observed rotational constants. A similar situation has been reported for nitrosyl bromide.[1]

To overcome this difficulty the species $N^{18}OCl$ has been prepared, and its microwave spectrum analysed. By combining the rotational constants thus obtained with those derived from the microwave spectra of $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$ the structural parameters have been determined. The orientation of the principal axes of inertia with respect to the

Table 1. *Spectrum of* $N^{16}O^{35}Cl$. *Assignments, relative intensities, and comparisons of observed and calculated frequencies.* (F_f *and* F_i *are the final and initial total angular momentum quantum numbers.*)

J' ← J	F_f ← F_i	Frequency (Mc./sec.) obs.	calc.	Relative intensity
$1_{01} \leftarrow 0_{00}$	3/2 ← 3/2	11,104·15	11,104·15	52·5
	5/2 ← 3/2	11,116·33	11,116·33	100·0
	1/2 ← 3/2	11,126·05	11,126·06	20·8
$2_{12} \leftarrow 1_{11}$	5/2 ← 3/2	21,857·42	21,857·32	52·5
	3/2 ← 3/2	21,860·70	21,860·67	26·7
	5/2 ← 5/2	21,864·59	21,864·57	22·5
	7/2 ← 5/2	21,869·39	21,869·40	100
	3/2 ← 1/2	21,873·93	21,873·90	20·8
	1/2 ← 1/2	21,879·07	21,878·73	20·8
$2_{02} \leftarrow 1_{01}$	5/2 ← 5/2	22,215·08	22,215·42	22·5
	3/2 ← 1/2		22,214·38	20·8
	5/2 ← 3/2	22,227·37	22,227·59	52·5
	7/2 ← 5/2		22,227·39	100
	3/2 ← 3/2	22,236·45	22,236·29	26·7
$2_{11} \leftarrow 1_{10}$	5/2 ← 3/2	22,580·47	22,579·78	52·5
	3/2 ← 3/2	22,585·47	22,585·03	26·7
	5/2 ← 5/2		22,584·60	22·5
	7/2 ← 5/2	22,592·95	22,591·95	100
	3/2 ← 1/2		22,593·71	20·8
	1/2 ← 1/2	22,601·72	22,601·06	20·8

[1] Weatherly and Williams, *J. Chem. Phys.*, 1956, **25**, 717.

TABLE 2. *Spectrum of* $N^{16}O^{37}Cl$. *Assignments, relative intensities, and comparison of observed and calculated frequencies.*

J'	J	F_f	F_i	Frequency (Mc./sec.) obs.	Frequency (Mc./sec.) calc.	Relative intensities
		3/2	3/2	10,849·36	10,849·37	52·5
1_{01}	0_{00}	5/2	3/2	10,858·96	10,858·97	100·0
		1/2	3/2	10,866·65	10,866·65	20·8
		5/2	3/2	21,362·64	21,362·06	52·5
		3/2	3/2	21,364·7	21,364·67	26·7
2_{12}	1_{11}	5/2	5/2	21,367·47	21,367·96	22·5
		7/2	5/2	21,371·53	21,371·66	100
		5/2	3/2	22,052·07	22,051·67	52·5
		3/2	3/2	22,056·03	22,055·88	26·7
		5/2	5/2		22,055·37	22·5
2_{11}	1_{10}	7/2	5/2	22,062·26	22,061·27	100
		3/2	1/2		22,062·54	20·8
		1/2	1/2	22,068·11	22,068·44	20·8
		5/2	5/2	21,703·77	21,703·77	22·5
		3/2	1/2		21,702·95	20·8
2_{02}	1_{01}	5/2	3/2	21,713·25	21,713·33	52·5
		7/2	5/2		21,713·33	100
		3/2	3/2	21,719·68	21,720·23	26·7

TABLE 3. *Spectrum of* $N^{18}O^{35}Cl$. *Assignments, relative intensities, and comparison of observed and calculated frequencies.*

J'	J	F_f	F_i	Frequency (Mc./sec.) obs.	Frequency (Mc./sec.) calc.	Relative intensity
		3/2	3/2	10,532·72	10,532·72	52·5
1_{01}	0_{00}	5/2	3/2	10,544·88	10,544·92	100
		1/2	3/2	—	10,554·68	20·8
		9/2	7/2		31,123·75	100
		5/2	5/2	31,123·80	31,124·96	14·6
3_{13}	2_{12}	3/2	1/2		31,123·67	28
		7/2	5/2	31,121·14	31,120·72	68·6
		5/2	3/2		31,120·63	44·8
		9/2	7/2	31,623·50	31,623·50	100
		7/2	5/2		31,623·50	68·6
		3/2	5/2	31,620·48	31,620·49	0·8
3_{03}	2_{02}	3/2	1/2		31,620·49	28
		7/2	7/2	31,611·34	31,611·37	11·4
		5/2	5/2	31,628·97	31,629·17	14·6
		3/2	3/2	31,632·28	31,632·62	11·2
		9/2	7/2	32,132·36	32,132·28	100
3_{12}	2_{11}	7/2	5/2	32,129·17	32,129·25	68·6
		5/2	3/2		32,129·25	44·8
		5/2	3/2	31,632·28	31,632·28	44·8
		3/2	3/2		31,632·28	11·2
2_{20}	3_{21}	7/2	5/2		31,623·58	68·6
		5/2	5/2	31,623·50	31,623·58	14·6
		3/2	5/2		31,623·58	0·8

molecular geometry has been settled at the same time. The nuclear quadrupole coupling coefficients which have been evaluated from the hyperfine structure refer to these axes, and the directional relationship had to be established before the nuclear quadrupole coupling could be related to bond properties.

The Spectrum.—The nitrosyl chloride molecule approximates closely to a near prolate symmetric rotor, the $\Delta J = 1$, $\Delta K = 0$ transitions falling in the regions of approximately 10, 20, and 30 kMc./sec. for $J,1 \leftarrow 0$, $2 \leftarrow 1$, and $3 \leftarrow 2$ transitions respectively. Because these lines are comparatively weak, a highly enriched (~90%) sample of the O^{18} species was prepared. The spectra of $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$ were observed by using a normal sample. The spectra showed quadrupole hyperfine structure arising from the chlorine nucleus, but that due to the nitrogen nucleus was not resolved. The frequencies

and assignments for the three isotopic species $N^{16}O^{35}Cl$, $N^{16}O^{37}Cl$, and $N^{18}O^{35}Cl$ are recorded in the Tables.

The values for the $J,2 \longrightarrow 1$ transitions of $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$ are in good agreement with those previously reported.[2] The observation of the $J,1 \longleftarrow 0$ transitions provides $B + C$ directly and leads to improved values for the nuclear quadrupole coupling coefficients.

The hyperfine structure may be described in terms of the coupling coefficients eQq_{aa}, eQq_{bb}, and eQq_{cc}, where e is the proton charge, Q the quadrupole moment of the chlorine nucleus, and q_{aa}, q_{bb}, and q_{cc} the molecular electric field gradients at the chlorine nucleus along the *a*-, *b*-, and *c*-axes of inertia. The hyperfine patterns were analysed according to first-order perturbation treatment for a near symmetric rotor.[3] It was found sufficient to retain only linear terms in the asymmetry parameter b. The coefficient eQq_{aa}, which refers to that principal axis, which is a near rotational symmetry axis, was obtainable directly from the $J,1 \longleftarrow 0$ transitions. The components of the higher J transitions were also used to obtain best values. Rotational transitions involving $K = 1$ levels have hyperfine structures which are determined in part by the remaining independent coefficient to be evaluated. For $N^{18}O^{35}Cl$ in which the transition $J,3 \longleftarrow 2$ was studied, eQq_{aa} was found to be −48·8 Mc./sec., but the splitting was too small to allow the other coefficients to be evaluated. The coefficients are given in Table 4.

TABLE 4. *Nuclear quadrupole coupling parameters.*

	eQq_{aa} (Mc./sec.)	eQq_{bb} (Mc./sec.)	eQq_{cc} (Mc./sec.)	η
$N^{16}O^{35}Cl$	−48·7	29·4	19·3	−0·207
$N^{16}O^{37}Cl$	−38·4	23·2	15·2	−0·207

The rotational constants were then calculated from the frequencies corrected for nuclear quadrupole perturbation. Values for $B + C$ were obtained directly from the $J,1 \longleftarrow 0$ transitions and confirmed by the $K = 0$ components of the $J,1 \longleftarrow 2$ transitions. The separation of the $K = 1$ components of $J,2 \longleftarrow 1$ or $3 \longleftarrow 2$ transitions yielded values for $B - C$. The rotational parameters are listed for the three molecular species in Table 5.

TABLE 5. *Rotational parameters.*

	C (Mc./sec.)	B (Mc./sec.)	A (Mc./sec.)	b
$N^{16}O^{35}Cl$	5376·39	5737·50	85,420	$-2·261 \times 10^{-3}$
$N^{16}O^{37}Cl$	5256·17	5600·88	85,400	$-2·155 \times 10^{-3}$
$N^{18}O^{35}Cl$	5103·17	5439·31	82,580	$-2·174 \times 10^{-3}$

No transition was observed from which the large rotational constant could be evaluated directly; the value reported is that calculated on the basis of a rigid planar molecule. The asymmetry parameter b has been calculated on the same assumption. The moments of inertia calculated from these values are given in Table 6. Tables 1, 2, and 3 show that the frequencies calculated in terms of these rotational parameters and the nuclear quadrupole coupling coefficients in Table 4 are in close agreement with the observed frequencies.

TABLE 6. *Moments of inertia* (a.m.u. Å^2).

	I_c	I_b	I_a
$N^{16}O^{35}Cl$	94·0283	88·1103	5·9180
$N^{16}O^{37}Cl$	96·1786	90·2592	5·9194
$N^{18}O^{35}Cl$	99·0621	92·9403	6·1219

Molecular Structure.—A knowledge of the change of molecular moments of inertia produced by isotopic substitution of both chlorine and oxygen makes it possible to determine the structure without recourse to the moments themselves.[4] Both co-ordinates

[2] Rogers, Pietenpol, and Williams, *Phys. Rev.*, 1951, **83**, 431.

[3] Knight and Feld, *Phys. Rev.*, 1948, **74**, 354A; Schwendeman, "A Table of Coefficients for the Energy of a Near Symmetric Top." See *J. Chem. Phys.*, 1959, **27**, 986.

[4] Kraitchman, *Amer. J. Phys.*, 1953, **21**, 7; Costain, *J. Chem. Phys.*, 1958, **29**, 864.

of the oxygen atom, referred to principal axes of inertia, can be determined directly from the inertial changes produced by ^{18}O substitution. Only a single co-ordinate of the chlorine atom can be settled in this way, since this atom is so close to the *a*-axis that the change in I_a on substitution is extremely small. The remaining chlorine atoms co-ordinate and both those of the nitrogen atom may be fixed by the first- and second-moment equations $\sum m_i x_i = \sum m_i y_i = \sum m_i x_i y_i = 0$, x_i and y_i being the in-plane co-ordinates referred to principal axes.

The structure obtained in this way is not as sensitive to small changes in the moments as is that obtained by using only information on $N^{16}O^{35}Cl$ and $N^{16}O^{37}Cl$. If errors of $\pm 0{\cdot}10$ Mc./sec. are assigned to the rotational constants B and C, then permutation over all combinations of values for the three isotopic species yields a structure within the range:

$$r_{NCl} = 1{\cdot}975 \pm 0{\cdot}005 \text{ Å} \quad r_{NO} = 1{\cdot}139 \pm 0{\cdot}012 \text{ Å} \quad \angle ONCl = 113° 20' \pm 40'$$

It is difficult to be certain what error should be ascribed to the rotational constants, for, although the comparison of calculated and observed frequencies in Table 1, 2, and 3 indicates a value of about $\pm 0{\cdot}10$ Mc./sec., there may be some undetected effect arising from the presence of unresolved nitrogen hyperfine structure, but from the width of the lines this seems unlikely to be serious. The structure is that which satisfies the changes in B and C on isotopic substitution. Because of a lack of direct information about A, it has not been possible to obtain the inertial defect and use it to gain an idea of the effect of zero-point motion on the parameters obtained.

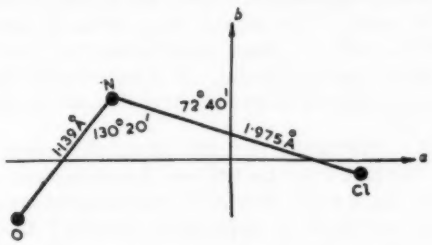

FIG. 1. *Structure and principal axes of the nitrosyl chloride molecule.*

The orientation of the principal axes for the $N^{16}O^{35}Cl$ molecule is shown in Fig. 1. It is these axes to which the nuclear quadrupole coupling coefficients in Table 4 refer. By making the assumption that the N–Cl bond is a principal axis of the coupling tensor, the coupling coefficients along and perpendicular to the bond have been found. Comparison is made in Table 7 with the coefficients for NO_2Cl, the only other molecule containing an N–Cl bond for which such information is available.[5]

TABLE 7. *Comparison of* ^{35}Cl *nuclear quadrupole coupling parameters.* (x *refers to the* N–Cl *bond-direction*; y *and* z *are the in- and out-of-plane perpendiculars respectively. All values are given in* Mc./sec.)

	χ_{xx}	χ_{yy}	χ_{zz}	$\chi_{yy} - \chi_{zz}$
NOCl	−57·2	37·9	19·3	18·6
NO_2Cl	−94·28	51·23	43·05	8·18

The coupling coefficients for nitryl chloride are derived directly from the experimental data, since in this case the N–Cl bond direction is also a principal axis of inertia, and there can be no doubt about the deviation from axial symmetry reflected in the difference between χ_{yy} and χ_{zz}. The effect has already been interpreted as indicating about 5% double-bond character.[5] The χ-values for nitrosyl chloride do not have quite the same status since, in this case, they have been obtained by a transformation of the coefficients along the principal axes of inertia, on the assumption that the N–Cl direction is a principal

[5] Millen and Sinnott, *J.*, 1958, 350.

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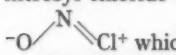
axis of the quadrupole coupling tensor. The dependence of the difference $\chi_{yy} - \chi_{zz}$ on the angle θ assumed between the tensor axis and the NCl direction is as follows: *

θ	$-3°$	$-2°$	$-1°$	0	$+1°$	$+2°$	$+3°$
$\chi_{yy} - \chi_{zz}$ (Mc./sec.).....	15·6	16·5	17·5	18·6	19·8	21·1	22·5

Negative values of θ indicate a direction corresponding to a bent bond bowing in towards the oxygen atom. This supposition would reduce somewhat the double-bond character as indicated by $\chi_{yy} - \chi_{zz}$. No assumption regarding θ will reduce the difference below 10 Mc./sec., and this minimum value is attained for the highly unlikely situation where $\theta = 14° 23'$, for which the tensor axes coincide with the inertial axes. It appears that the N–Cl bond has a greater double-bond character for nitrosyl chloride than for nitryl chloride; when θ is taken as zero the double-bond character as measured by electron-loss from the p_z orbital is found to be 10·3%.

An even more striking difference between the two chlorides is that in the field gradients along the bonds. A much greater ionic character for nitrosyl chloride is clearly indicated. If the chlorine orbital used in bond formation is taken as pure $3p$ and the importance of the overlap integral may be neglected in normalisation, then the importance of the ionic contribution NO^+Cl^- is found to be approximately 40%. The two assumptions made here operate in opposite directions, and probably have a better justification in this case than for most bonds. The bond is long (1·975 Å) and so, first, the overlap integral is reduced, and secondly, overlap considerations do not favour appreciable *s*-hybridisation of the chlorine bonding orbital. It is noteworthy that the higher ionic character (NO^+Cl^-) for nitrosyl chloride than for nitryl chloride is accompanied by larger double-bond character



which partially offsets the charge separation.

The high value for the bond length is itself, of course, an indication of the importance of ionic character.[6] Few N–Cl bond lengths are available for comparison. That in Me_2NCl ($r_{N-Cl} = 1·77$ Å) is appreciably shorter,[7] though this may be due partly to different hybridisation about the nitrogen atom. Comparison with nitryl chloride ($r_{N-Cl} = 1·840$ Å) is probably better since the ∠ONCl angles for both molecules are very similar. The increase of 0·14 Å in passing from nitryl to nitrosyl chloride is taken to be an indication of the much greater ionic contribution in the latter case.

The ionic character is also reflected in the N–O bond stretching force constant. A value of 14*md*/Å has been reported[8] for nitrosyl chloride. According to a correlation[9] which has been made for N–O bond stretching force constants, this indicates an N–O bond order of about 2·4.

Experimental

Preparation of $N^{18}OCl$.—*Electrolytic preparation of* ^{18}O*-enriched oxygen.* The route used for the preparation of nitrosyl chloride containing approximately 90% of ^{18}O was to use oxygen prepared by the electrolysis of ^{18}O-enriched water for the oxidation of ammonia and then to cause the resulting oxides of nitrogen to react with hydrogen chloride.

An electrolytic cell (Fig. 2) was designed to electrolyse about 0·6 ml. of water, leaving a residue of less than 0·1 ml. The cell consists of a 3 cm. length of capillary tubing (2 mm. internal diameter) bent to form a U-tube, which is connected to wider-bore tubing (6 mm. internal diameter) which contains nearly the whole of the water to be electrolysed. (The capacity of the U-tube is 0·09 ml.) Electrodes are provided as platinum wires which extend past the capillary tube.

* Since the measured coefficients for $N^{18}OCl$ and $N^{16}OCl$ refer to different inertial axes it might be thought that the coefficients for the two molecules determine θ. However, the principal axes are rotated only by about 40′ on ^{18}O-substitution and the effect on the eQq's is too small to be of use.

[6] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.
[7] Stevenson and Schomaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1813.
[8] Burns and Bernstein, *J. Chem. Phys.*, 1950, **18**, 1669; Landau and Fletcher, *J. Mol. Spectroscopy*, 1960, **4**, 276.
[9] Millen, Polydoropoulos, and Watson, *J.*, 1960, 687.

In operating the cell, electrolytic hydrogen and oxygen were collected in flasks connected to the appropriate limbs. It was necessary during the collection of the gases to avoid building up even a small pressure difference across the cell, for this would displace the electrolyte and reduce the fraction which could be electrolysed. For this purpose a differential device illustrated in Fig. 3 was connected to the collecting flasks and to the electrolytic cell at the points marked A. It consists of 200 ml. flasks inserted into each arm and interconnected by a three-way tap. Each flask is half-filled with silicone oil, thus providing a collecting volume of approximately 800 ml. for hydrogen and 400 ml. for oxygen. These volumes were made as closely as possible in the ratio 2 : 1. Because of the large surface area of the silicone oil a small pressure change will correct for any small deviation from the volume ratio 2 : 1. The device has a differential-volume change of approximately 60 ml. per mm. Hg difference in pressure.

Approximately 0·7N-sodium hydroxide was used as electrolyte. This was prepared by using a capillary-tube technique to dissolve oxide-free sodium in the enriched ^{18}O water. It was found in a number of exploratory runs with normal water that more dilute solutions suffered

FIG. 2. *The electrolytic cell.*

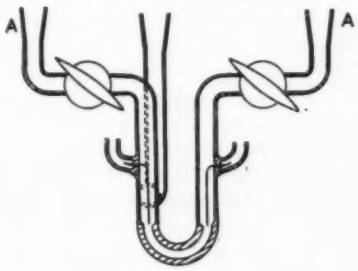
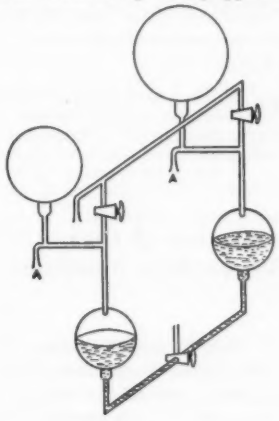


FIG. 3. *Pressure-equalising apparatus.*



from disadvantages: first, the greater electrolytic heating led to a tendency to bubble formation which often stopped the electrolysis; secondly, concentration polarisation caused the current to decrease after a time. Even with the more concentrated solution it was necessary temporarily to close one of the taps from time to time and thus overcome concentration polarisation by mixing the electrolyte. A current of about 50 mA was found suitable, and although only about 1 watt was dissipated in the cell it was cooled in ice-water, as this was found to reduce the possibility of bubble formation, which led to interruption of the electrolysis. The total quantity of electricity passed was recorded in order to calculate the amount of oxygen obtained.

Before electrolysis was started, the silicone oil was carefully out-gassed, and the apparatus evacuated. Finally, it was found helpful to introduce about 20 cm. Hg pressure of oxygen-free nitrogen into the apparatus before starting the electrolysis, otherwise undesirable frothing of the electrolyte occurred.

Oxidation of ammonia. Oxygen and ammonia were mixed, passed *via* a flow-meter over heated catalyst, and the products collected. Numerous trial runs were made to find most the favourable conditions. The main problem was to avoid the formation of nitrous oxide and ammonium nitrate or nitrite which represented a loss of oxygen. The main conclusions which are consistent with those reached by Zawadzki [10] from experiments under somewhat different conditions are that the formation of nitric oxide is favoured by (*a*) a high flow rate through the catalyst, (*b*) a high temperature, and (*c*) a short catalyst bed. There were also indications that increasing the proportion of ammonia in the mixture favoured the formation of nitrous oxide.

In the final form of the apparatus a catalyst chamber of fused silica was packed with platinised asbestos for a length of 5 cm. and provided with a heater to operate at about 600° C;

[10] Zawadzki, *Discuss. Faraday Soc.*, 1950, **8**, 140.

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225 ml. of oxygen at N.T.P. were mixed with 150 ml. of ammonia at N.T.P. and passed over the catalyst, and the product, consisting mainly of dinitrogen tetroxide and a little dinitrogen trioxide, was condensed at −190° c. Excess of hydrogen chloride was admitted and after the reaction was complete the nitrosyl chloride was separated by distillation.

Normal Nitrosyl Chloride.—This was prepared by passing pure nitrogen dioxide through a column of moist potassium chloride.

Observation of Spectra.—Spectra were observed by using a Stark-modulated spectrometer whose main constructional features have been described previously.[5] The absorption cells were cooled in solid carbon dioxide and the sample flowed through continuously. For much of the work 2K33 klystrons were used, and some use was made of R5222 tubes in the various available interchangeable cavities. For the region above 30 kMc./sec. E.M.I. klystrons VX 5023 were employed. The observation of several lines in the region 10—11 kMc./sec. was made possible by the use of the E.M.I. klystron cavity type 25182.

We are indebted to the University of London for the award of a Studentship Grant (to J. P.), to Dr. I. Dostrovsky, of the Weizmann Institute of Science, for arranging the supply of 89% ^{18}O-enriched water, and to E.M.I. for a prototype klystron cavity type 25182. We appreciate the continued interest of Professor Sir Christopher Ingold, F.R.S., and Professor E. D. Hughes, F.R.S.

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255. *Solvation of Ions. Part II.*[1] *Dipolar Aprotic Solvents as Media for Nucleophilic Substitution Reactions at a Saturated Carbon Atom.*

By A. J. Parker.

Kinetic experiments on the S_N2 reactions of methyl iodide with lithium chloride, tetraethylammonium (or sodium) azide, sodium picrate, sodium cyanide, potassium fluoride, potassium thiocyanate, and lithium bromide severally, in the protic solvents methanol, 10% dioxan–formamide, and *N*-methylformamide, and in the dipolar aprotic solvents dimethylformamide, dimethylacetamide, and acetone are reported. The solvolysis rates of methyl iodide in these solvents and the rate of S_N2 decomposition of trimethylsulphonium bromide in dimethylformamide have also been measured.

S_N2 rates increase by a factor of up to 10^7 as the hydrogen-bonding capacity of the solvent decreases from water to dimethylacetamide through a series of methyl-substituted amides, but solvolysis rates are little influenced by solvent change. Acetone is confirmed as a typical dipolar aprotic solvent.

The observed effects of solvents on rates are due to solvation differences, in the two types of solvent, of the anionic participants, not of the organic substrates.

Halogen and halogenoid ions in the absence of differential solvation (*i.e.*, deactivation) due to hydrogen bonding, have similar nucleophilic tendencies. A reappraisal of current ideas on nucleophilic tendency must be made. In dimethylformamide, reactivity towards methyl iodide is in the order $CN^- > F^-, Cl^-, N_3^-, Br^- > SCN^- >$ Picrate$^-$.

Some examples of increased yields and shorter reaction times, when dipolar aprotic solvents are the reaction media, are explained by a simple postulate.

Miller and Parker[1] have reported that aromatic nucleophilic substitution (S_NAr) reactions are up to 10^5 times faster in nine dipolar aprotic solvents than they are in three protic solvents. Rate constants (k_2) increased as the hydrogen-bonding capacity of the

[1] Part I, Miller and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 117.

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solvent decreased from methanol to dimethylacetamide. It was suggested that in dipolar aprotic solvents solvation of anions is in the reverse order to that accepted for protic solvents, *i.e.*, solvation decreases in the series of anions

$$\text{Transn. state ion} > \text{Picrate}^- > I^- > SCN^- > Br^- > N_3^-, Cl^- \gg F^-$$

We felt that this effect on rate, in the change from protic to dipolar aprotic solvent, should be general for anion–dipolar molecule reactions passing through a relatively large, negatively charged transition state. This work shows that such solvent influence is general for bimolecular nucleophilic substitutions such as (1) and (2):

$$R{-}X + Y^- \longrightarrow RY + X^- \quad (1)$$

$$R{-}X^+ + Y^- \longrightarrow RY + X \quad (2)$$

where R = alkyl or aryl. R was chosen as methyl for the new results because it is the simplest for displacements at carbon, and because higher homologues eliminate HX readily in dipolar aprotic solvents.[2]

Reactions of Y^- have been studied to estimate qualitatively the effect of anion size, basicity, and polarizability on relative solvation, and thus reactivity, of anions in protic and dipolar aprotic solvents. It was hoped that the effect on rate, of solvation of Y^-, of RX, and of the transition state $[Y \cdots R \cdots X]^-$ in reaction (1), could be separated by varying RX in some series in which Y^- was constant.

It has been apparent for some years that the results of Ingold and his co-workers for rates of Finkelstein substitutions in acetone [3] can be used to calculate semi-quantitative rate constants [4] which allow for incomplete dissociation of salts in acetone, and give as good a picture as possible of the nucleophilic tendency of " free " halide ions in acetone. Winstein [5] has recently done this. The derived values of halides in acetone agree with those now experimentally observed in dimethylformamide.

The principles discussed here and in Part I explain some examples of increased yields and shorter reaction times in dipolar aprotic solvents. These hitherto unconnected examples are being reported more frequently and it is hoped that this series of papers will enable one to select the most suitable solvent in given circumstances.

Results and Discussion

Table 1 records rate constants and solvent rate ratios for nucleophilic substitutions in various solvents. Anionic nucleophiles used were azide ion, a strong base in water and methanol, and chloride ion, a weak base in water and methanol. Both are strong bases in dipolar aprotic solvents [6] and form relatively strong bonds with carbon. Substrates were methyl iodide, which is slowly solvolysed by some solvents, and *p*-fluoronitrobenzene, which was recovered quantitatively from the solvents at the temperature used.[1] These are two of the simplest substrates for S_N2 and S_NAr reactions respectively. Displaced groups were weakly bound (iodide), and strongly bound (fluoride) to carbon.

The solvents methanol, formamide (I), *N*-methylformamide (II), *NN*-dimethylformamide (III), dimethylacetamide (IV), and acetone should form hydrogen bonds with a suitable anion in the order, MeOH > (I) > (II) ≫ (III) > (IV), $COMe_2$. In this work 10% dioxan–formamide was used since methyl iodide is only slightly soluble in formamide. This amount of dioxan does not greatly affect rates in methanol and water,[1] so it is assumed that rates in formamide and in 10% dioxan–formamide are comparable.

[2] Parker and Hughes, unpublished work.
[3] de la Mare, Hughes, Ingold, *et al.*, *J.*, 1955, 3169—3200.
[4] Hughes, Ingold, and Parker, *J.*, 1960, 4400.
[5] Winstein, Savedoff, Smith, Stevens, and Gall, *Tetrahedron Letters*, 1960, No. 9, 24.
[6] Janz and Danyluck, *Chem. Rev.*, 1960, **60**, 209.

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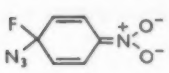
TABLE 1. *Rate constants* (10^4k_2, l. mole^{-1} sec.$^{-1}$) *at temperature shown for the reactions* (A) $CH_3I + LiCl \rightleftharpoons CH_3Cl + LiI$, (B) $p\text{-}NO_2\cdot C_6H_4F + NEt_4N_3 \longrightarrow p\text{-}NO_2\cdot C_6H_4\cdot N_3 + NEt_4F$ *in various solvents.* [*Equimolar concentrations* (0·035—0·045M) *of reactants for all new results. Solvolysis rates* (*expressed as* 10^6k_1 [a]) *at* 25·1° *for methyl iodide at an initial concentration of* 0·050—0·057M.]

	Reaction A		Ratio $\frac{k_2\text{ (solvent)}}{k_2\text{ (water)}}$		Reaction B		Ratio $\frac{k_2\text{ (solvent)}}{k_2\text{ (methanol)}}$		Solvolysis
Solvent	10^4k_2	T	0°	25°	10^4k_2	T	25°	100°	10^6k_1
H_2O	0·0011 [c]	0·0°	1	—	—	—	—	—	
H_2O	0·032 [c]	25·1	—	1	—	—	—	—	0·1 [d]
MeOH	0·030	25·1	—	0·94	$6·7 \times 10^{-4}$	25·1°	1	—	
MeOH	—	—	—	—	2·28	100·0	—	1	4×10^{-3} [g]
10% Dioxan–formamide...	0·40 [e]	25·1	—	12·5	13·0	100·0	—	5·6	1·0
N-Methyl-formamide...	1·45 [e]	25·1	—	45·3	36·0	100·0	—	15·7	1·1
$NMe_2\cdot CHO$ ...	1300	0·0	$1·2 \times 10^6$	—	16·4	25·1	$2·45 \times 10^4$	—	0·28
$NMe_2\cdot CHO$ ...	—	—	—	—	11,100	100·0	—	$4·9 \times 10^3$	—
$NMe_2\cdot COMe$ ...	8100	0·0	$7·4 \times 10^6$	—	59	25·1	$8·8 \times 10^4$	—	0·26
$COMe_2$	50,000 [f]	25·1	—	$1·6 \times 10^6$	47·4	25·1	$2·45 \times 10^4$	—	—

[a] See p. 1331. [b] Results from Part I. [c] Bathgate and Moelwyn-Hughes, *J.*, 1959, 2642. [d] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295. [e] Results corrected to allow for solvolysis reaction (see text). [f] Calculated from the observed rate at 50% reaction (ref. 4) divided by the concentration of methyl iodide and of free chloride ions (see p. 1331), *i.e.* $k_f = k_2/\alpha$. The recorded rate constant is k_f, the rate constant for attack by free chloride ions, and k_2 is the observed rate constant calculated from stoicheiometric concentrations of reactants in the normal way; α is the degree of dissociation at 50% reaction calculated from the dissociation constants in acetone at 25°: $K_{LiCl} = 2·03 \times 10^{-5}$, $K_{LiI} = 2·85 \times 10^{-3}$. [g] Extrapolated from the observed k_1 of $2·0 \times 10^{-7}$ sec.$^{-1}$ (Table 7) to give this semiquantitative figure. The recorded result is satisfactory for the discussion.

S_NAr reactions between *p*-fluoronitrobenzene and azide ion (Reaction B, Table 1) stop at the intermediate complex (V) in dipolar aprotic solvents, but fluoride is removed by protic solvents.[1] The S_N2 LiCl–CH_3I exchange proceeds at least 95% in the forward direction in all solvents,[4] except where solvolysis interferes. Table 1 includes rates $d[I^-]/dt$, expressed as k_1, for solvolysis of methyl iodide at an initial concentration of 0·02M, measured over the first 30% of reaction. The k_1 values are not constant (Table 8), but the downward drift is not more than 50%; however, as will be seen, they are satisfactory for our purpose.



(V)

Table 2 gives k_2 values and solvent rate ratios for a variety of S_N2 and S_NAr reactions in dimethylformamide and methanol. All substrates and salts used were recovered from either solvent when treated separately with solvent for a period corresponding to reaction conditions of Table 2. The CH_3I–LiBr exchange had an equilibrium constant of 8·5 in

TABLE 2. *Rate constants* (10^5k_2, l. mole^{-1} sec.$^{-1}$) *at* 0° *unless otherwise stated, for some* S_N2 *and* S_NAr *reactions in methanol and dimethylformamide.*

Reactants	10^5k_2 in methanol	$NMe_2\cdot CHO$	Ratio $\frac{k_2\text{ (}NMe_2\cdot CHO\text{)}}{k_2\text{ (methanol)}}$
CH_3I + LiBr	0·183 [d]	10,700	$5·8 \times 10^4$
$Me_3S^+Br^-$ [a]	0·0035 [b,c]	125 [b]	$3·5 \times 10^4$ [b,c]
CH_3I + KSCN	2·0	1100	$5·5 \times 10^2$
$2,4\text{-}(NO_2)_2C_6H_3I$ + KSCN [a]	0·017	1·08	$6·5 \times 10^1$
CH_3I + NaN_3	0·30	13,800	$4·5 \times 10^4$
$p\text{-}NO_2\cdot C_6H_4I$ + NaN_3 [a]	$4·4 \times 10^{-7}$	0·020	$4·6 \times 10^4$
$p\text{-}NO_2\cdot C_6H_4F$ + NaN_3 [a]	$1·55 \times 10^{-4}$	7·86	$5·0 \times 10^4$

[a] At an ionic strength of 0·08M, buffered with 0·04M-$LiClO_4$. [b] At 59·8°. Calc. for a hypothetical alcoholic solvent of the same dielectric constant as D.M.F. (see p. 1331). [c] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1939, **35**, 368. [d] Data calculated from the Arrhenius parameters given in Part I.

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dimethylformamide at 0·0° (Table 5), and the decomposition of trimethylsulphonium bromide (Table 6) appeared to come to equilibrium also. For these reactions, rate constants were calculated over the first 40% of reaction. Other reactions proceeded to more than 70% completion.

Decomposition of trimethylsulphonium bromide is very susceptible to the ionic strength and the dielectric constant (D) of the medium.[2] The k_2 value in Table 2 for " methanol " is calculated from initial k_2 values in ethanol and methanol [2,7] at an ionic strength of 0·08M (buffered with 0·04M-lithium perchlorate) by extrapolation of a log k_2–$1/D$ plot [8] to the dielectric constant ($D = 37·6$) of dimethylformamide.[9] The measured k_2 in dimethylformamide is compared with this hypothetical k_2 for the decomposition of trimethylsulphonium bromide in a hydroxylic solvent of the same dielectric constant at the same ionic strength.

Table 3 records k_2 and solvent rate ratios for S_N2 reactions of methyl iodide with some nucleophiles in methanol, water, dimethylformamide, and acetone. Swain and Scott's [10] nucleophilic constants η are included for comparison.

Table 4 gives semiquantitative specific rate constants, k_i, calculated from the rates of Ingold *et al.*[3] for Finkelstein reactions in acetone. Acree's formula,[11] in the absence of a better one, has been used to calculate k_i, which is the second-order rate constant for attack by " free " halide ions: *i.e.*, $k_i = k_2/\alpha$, where k_i = specific rate constant, k_2 = observed rate constant, and α = degree of dissociation of LiHal. Values of α were calculated from the mass-law expression with appropriate salt concentrations at 50%

TABLE 3. *Anion nucleophilicity towards methyl iodide. Rate constants (k_2, l. mole^{-1} sec.$^{-1}$) at temperature shown for the reaction* $CH_3I + Y^- \longrightarrow CH_3Y + I^-$ *in protic and dipolar aprotic solvents. Equimolar concentrations (0·035—0·045M) of reactants for all new results. Comparison with Swain and Scott's nucleophilic constants η,[a] and effect of solvent change on different anions.*

	η [a] of Y^-	$10^5 k_2$ at 0° in MeOH	$10^5 k_2$ at 0° in H_2O	$10^1 \times k_2$ at 0° in NMe_2·CHO	k_2 (NMe_2·CHO) / k_2 (Protic) at 0°	k_2 ($COMe_2$) [b] / k_2 (H_2O) at 25°
Na picrate ...	1·9	1·8 [b]	—	$3·6 \times 10^{-3}$ [b]	20 [b]	—
KSCN	4·77	2·0	—	0·11	$5·5 \times 10^3$	—
LiI	5·04	—	1·6 [c]	—	—	$2·5 \times 10^4$
LiBr.....	3·89	—	0·18 [c]	1·07	$5·5 \times 10^4$	$2·1 \times 10^5$
NaN_3	4·00	0·30	—	1·36	$4·5 \times 10^4$	—
NaCN	5·10	—	2·3 [f]	>10 [g]	$>5 \times 10^4$	—
LiCl	3·04	0·01	0·010 [c]	1·30	$1·3 \times 10^6$	$1·5 \times 10^6$
KF	2·0	—	7×10^{-3} [c,e]	>1 [c,d]	$>10^8$ [c]	—

[a] Refs. 9 and 10. [b] At 59·8°. [c] At 25°. [d] Estimated from the half-life of 5—10 min. (depending on stirring efficiency) for formation of iodide ion from 0·04M-CH_3I and 1 g. of finely divided solid KF suspended in dimethylformamide. [e] Ref. (*c*), Table 1. [f] Moelwyn-Hughes and Marshall, *J.*, 1959, 2640. [g] Reaction was complete 1 min. after mixing at 0·0°: equimolar amounts of CH_3I and NaCN in dimethylformamide. [h] Rate ratios taken from Table 4.

reaction and allowance for common-ion effects, and from the dissociation constants at 25°, *viz.*, $K_{LiCl} = 2·03 \times 10^{-5}$,[12] $K_{LiBr} = 5·22 \times 10^{-4}$,[13] $K_{LiI} = 2·85 \times 10^{-3}$,[12] $(6·9 \times 10^{-3})$,[14] and $K_{LiClO_4} = 1·9 \times 10^{-4}$.[15] Incomplete dissociation of sodium, lithium, or tetraethylammonium salts at <0·04M does not affect rate constants by more than 10% in solvents of dielectric constant > 33.[1]

[7] Budd, Thesis, London, 1952; Whittingham, Thesis, London, 1950.
[8] Laidler, " Chemical Kinetics," McGraw-Hill, New York, 1950, p. 128.
[9] Hine, " Physical Organic Chemistry," McGraw-Hill, New York, 1956.
[10] Swain and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.
[11] Acree, *Amer. Chem. J.*, 1912, **48**, 353.
[12] Blokker, *Rec. Trav. chim.*, 1935, **54**, 975.
[13] Evans and Sugden, *J.*, 1949, 270.
[14] Unpublished work by Savedoff, quoted in ref. 5.
[15] Accascina and Sckiavo, *Ann. Chim.* (*Italy*), 1953, **43**, 695.

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All the new substitutions, like the quoted reactions, of Tables 1—4 followed second-order kinetics over not less than 40% of reaction and gave the expected substitution products. Solvolysis, in reactions of methyl iodide in *N*-methylformamide and 10% dioxan–formamide, and in methanol for the reaction with sodium picrate only, was a minor reaction (<20%) and could be allowed for by using the formula of Hughes, Ingold, and Shapiro,[16] since solvolysis rates are known (Table 1). Solvolysis rates of methyl iodide by methanol and by methanol containing 0·04M-lithium perchlorate were within 10% of each other (Table 7), so that k_1 for solvolysis by pure solvent can be used to separate S_N2 rates from the overall rate of iodide-ion production. In the other reactions, each iodide ion formed from methyl iodide corresponded to a chloride, bromide, thiocyanate, cyanide, or azide ion consumed. No acid was detected. It is concluded that all new k_2 values, like the literature values of Tables 1—4, are for bimolecular additions of an anion to carbon, usually followed or accompanied by displacement from that carbon atom of some other group or neutral molecule.

Some rate constants at 25° and 100°, which were not used in Tables 1—4, are in Table 9. The temperatures used are common when comparing rate data, and since Arrhenius parameters have not been included, the results may be of value to other workers.

The following points should be noted:

(1) The two reactions (A and B) of Table 1 have the same solvent behaviour, although reaction A is more sensitive than B. As hydrogen-bonding capacity decreases, rate constants increase, as shown below:

Solvent	MeOH	NH_2·CHO	NHMe·CHO	NMe_2·CHO	NMe_2·COMe	$COMe_2$
Rel. rates (reaction A) ...	1	12·5	45·3	$1·2 \times 10^6$	$7·4 \times 10^6$	$1·6 \times 10^6$
Rel. rates (reaction B) ...	1	5·6	15·7	$2·4 \times 10^4$	$8·8 \times 10^4$	$2·4 \times 10^4$

(2) Specific rate constants for the reactions of " free " halide ions in acetone recorded in Tables 1, 3, and 4 suggest that acetone is a typical dipolar aprotic solvent like dimethylformamide and -acetamide, nitrobenzene, and the other solvents described in Part I.

TABLE 4. *Specific and observed rate constants (k_i and k_2, l. mole^{-1} sec.$^{-1}$) for Finkelstein substitutions in acetone and water at 25°.*

	[LiHal] (M)	α [a]	10^4k_2 [a] ($COMe_2$)	10^4k_i ($COMe_2$)	10^4k_2 [b] (H_2O)	k_i ($COMe_2$) / k_2 (H_2O)
$CH_3Cl + Cl^-$	0·0275	0·027	0·388	14	0·0055	2500
$CH_3Br + Cl^-$	0·0503	0·010	59·5	5,950	0·046	$1·3 \times 10^4$
$CH_3I + Cl^-$	0·0246	0·004	176 [c]	47,000	0·032	$1·5 \times 10^6$
$CH_3Cl + Br^-$	0·0240	0·10	3·4	34	0·17	200
$CH_3Br + Br^-$	0·0240	0·10	1300	13,000	—	—
$CH_3I + Br^-$	0·0220	0·03	2700	90,000	0·44	$2·1 \times 10^5$
$CH_3Cl + I^-$	0·0365	0·34	—	16 [d]	0·20	80
$CH_3Br + I^-$	0·0220	0·36	2500	7000	7·02	1000
$CH_3I + I^-$	0·100	0·24	20,000	80,000	3·3	$2·5 \times 10^4$ [e]
$CH_3Br + F^-$	—	—	3400 [f]	>3400	$4·6 \times 10^{-4}$	$>8 \times 10^6$

[a] Data from ref. 3 unless stated otherwise. [b] Data from Bathgate and Moelwyn-Hughes, *J.*, 1959, 2642 unless stated otherwise. [c] Ref. 4. [d] Aziz and Moelwyn-Hughes, *J.*, 1959, 2636. [e] α, the degree of dissociation of LiHal in acetone, has been calculated at 50% reaction with due allowance for the effect on α of the product LiHal, and of any added buffer salts, *e.g.*, $LiClO_4$, using the dissociation constants for salts in acetone given in the text. [f] Rimmer, unpublished work, quoted by Mackie, Thesis, London, 1955; α is not known and k_i is a minimum value. [g] This value agrees with that of Swart and Le Roux, *J.*, 1957, 406.

(3) Solvolysis rates of methyl iodide recorded in Table 1 exclude the possibility that an S_N1, or other process not dependent on the nucleophile, accounts for the observed rates. Solvent effects are similar for S_NAr and S_N2 reactions in a number of structurally different dipolar aprotic solvents,[1] which suggests that it is not a reactive CH_3I–solvent adduct which is reacting in the S_N2 process.

The mechanism of solvolysis was not studied, but amide solvolysis may involve

[16] Hughes, Ingold, and Shapiro, *J.*, 1936, 225.

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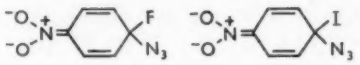
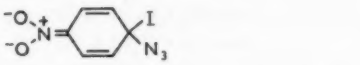
reversible formation of a quaternary salt, followed by decompositions, either ***in situ*** or after water is added.[17] Solvolysis rates decrease by a factor of 20 from water to dimethylacetamide, but S_N2 rates increase by 10^7. The conclusion is that differential solvation of the forming iodide ion in solvolysis of methyl iodide is not very important to the rate, and that the enormous S_N2 solvent effect must be a property of relative nucleophile and/or transition-state solvation, rather than of solvation of methyl iodide.

(4) Table 2 suggests that the solvent effect is associated with only the anionic nucleophile rather than with the transition state or substrate. The transition states:

$[N_3\cdots CH_3\cdots I]^-$  

seem to be equally susceptible to the change of solvent from methanol to dimethylformamide, as do:

$[Br\cdots CH_3\cdots I]^-$ and $[Br^{\delta-}\cdots CH_3\cdots {}^{\delta+}SMe_2]$

However, the derived k_i values of Table 4 show that susceptibility to solvent is in the order MeI $\gg$ MeBr $>$ MeCl. The explanation may be that, in the reactions of Table 2, solvation of the leaving group is either not a kinetically significant step (*e.g.*, S_NAr reactions of anions other than thiocyanate [18]) or is not very different in protic or in dipolar aprotic solvents (as is the case with iodide ion [1] or dimethyl sulphide as leaving group). In such reactions, solvent effects will be mainly a function of solvation of the attacking anion. In S_N2 reactions of methyl chloride and, to a smaller extent, of the bromide, solvation of the departing halide ion, which decreases the energy of the transition state, is very much greater because of hydrogen bonding in protic than in dipolar aprotic solvents. The argument is summarized by the annexed scheme.

Qualitative representation of solvation energies in protic and dipolar aprotic solvents (X = I or Cl).

Since a well-solvated transition state increases rate, and strong solvation of Y^- decreases rate, it is apparent why methyl iodide is more susceptible to solvent change than is methyl chloride in S_N2 reactions. Reactions of methyl iodide should give a better picture of relative solvation of nucleophiles unobscured by transition-state effects than reactions of other methyl halides.

(5) Chloride ion is more susceptible to solvent change than the stronger base, azide ion (Table 3). This confirms that hydrogen bonding to smaller, densely charged anions, and not an acid–base interaction in water, reduces the reactivity of anions in protic solvents and accounts for the differences in solvation in protic and dipolar aprotic solvents.

The anions of Table 3 are susceptible to solvent change in the order, $F^- > Cl^-$, $CN^- > Br^-$, $N_3^- > I^- > SCN^-$ > Picrate$^-$. This corresponds roughly with their increasing size and polarizability and decreasing tendency to form hydrogen bonds with protic solvents. The order is the reverse of their expected interactions with dipolar aprotic solvents and fits the degrees of anion solvation shown in Fig. I of Part 1.[1]

[17] Kornblum and Blackwood, *J. Amer. Chem. Soc.*, 1956, **78**, 4037.
[18] Parker, "Sulfur Nucleophiles in S_NAr Reactions," in "Organic Sulfur Compounds," Pergamon, London, 1960.

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(6) Nucleophilicity in dimethylformamide towards methyl iodide at 0·0° decreases, as shown in Table 3, in the order, $CN^- > F^-$, Cl^-, N_3^-, $Br^- > SCN^- >$ Picrate$^-$, relative rates being > 10, > 1, 1, 1, 1, 0·1, 0·004.

The nucleophilic tendencies of chloride, bromide, and iodide ions in acetone (Table 4), although not precisely observed values, follow a similar pattern to those in dimethylformamide. Thus in acetone (relative rates in parentheses) the apparent nucleophilic tendency at 25°

towards CH_3I is Br^- (2), I^- (2) $> Cl^-$ (1);
towards CH_3Br is Br^- (2) $> I^-$ (I), Cl^- (1);
towards CH_3Cl is Br^- (2) $> I^-$ (1), Cl^- (1);
towards butyl *p*-bromobenzenesulphonates [5] is Cl^- (17) $> Br^-$ (3) $> I^-$ (1).

Winstein [5] has commented recently on nucleophilic tendencies in acetone.

Reassessment of current ideas is called for. Nucleophilic tendencies in dimethylformamide and other dipolar aprotic solvents cannot be correlated with Swain and Scott's nucleophilic constants,[10] or with relative rates towards methyl iodide in water [19] or towards the trimethylsulphonium ion in ethanol or methanol.[2]

It seems that sulphur nucleophiles, and others whose nucleophilic atoms are of high atomic number, are powerful nucleophiles in hydroxylic (protic) solvents simply because they do not form strong hydrogen bonds with the solvent, not because they are polarizable and can adjust their outer electron shell to the requirements of a " stable " transition state, as is generally assumed.[9,18] Fluoride and cyanide ions are strong nucleophiles, in the absence of deactivation by solvation, because they form strong bonds with carbon. It may be that polarizability should not be discounted entirely, since interactions of halides and related groups with electron-deficient atoms of dipolar aprotic solvents (which would reduce reactivity) should decrease in the order, $SCN^- > I^- > Br^-$, $N_3^- > Cl^- > F^-$. Such interactions could almost exactly cancel any advantage large anions might have, owing to their polarizability and diffuse orbitals, in forming bonds with electron-deficient carbon. This would explain the " common rate " for S_N2 reactions of a number of these ions in dimethylformamide and in acetone (Tables 3 and 4). Apparently dipolar aprotic solvents are levelling and protic solvents are differentiating for nucleophilic tendencies of anions, whereas it has been observed [6] that protic solvents are levelling and dipolar aprotic solvents are differentiating for basicity of anions towards the proton.

Our postulate,[1] that any bimolecular reactions of a small anion passing through a large polarizable transition state will be considerably accelerated in the change from protic to dipolar aprotic solvent, explains some examples of increased yields and shorter reaction times when dipolar aprotic solvents are used as the reaction medium: for the Gabriel phthalimide synthesis; [20] in alkylations of sodium acetylide,[21] of phenanthrene,[22] of phenothiazines,[23] of saccharin,[24] of 6-mercaptopurines,[25] and of imidazoles; [25] in diethyl malonate additions; [26] in synthesis of aromatic fluorides [27] and iodides,[28] of alkyl cyanates,[29]

[19] Bathgate and Moelwyn-Hughes, *J.*, 1959, 2642.
[20] Sheehan and Bolhofer, *J. Amer. Chem. Soc.*, 1950, **72**, 2786; Vassel, U.S.P. 1956, 2,757,198; Donahoe *et al.*, *J. Org. Chem.*, 1957, **22**, 68; Billman and Cash, *Proc. Ind. Acad. Sci.*, 1953, **62**, 158; *J. Amer. Chem. Soc.*, 1954, **76**, 1944; Lo and Shropshire, *J. Org. Chem.*, 1957, **22**, 999.
[21] Rutledge, *J. Org. Chem.*, 1959, **24**, 840, U.S.P. 2,846,491/1958.
[22] Nelson and Garland, *J. Amer. Chem. Soc.*, 1957, **79**, 6313.
[23] Zaugg, Swett, and Stone, *J. Org. Chem.*, 1958, **23**, 1389.
[24] Rice and Pettit, *J. Amer. Chem. Soc.*, 1954, **76**, 302.
[25] Johnston, Holum, and Montgomery, *J. Amer. Chem. Soc.*, 1958, **80**, 6265.
[26] Schudy and Collins, *J. Org. Chem.*, 1959, **24**, 556; Burgstahler and Aiman, *ibid.*, 1960, **25**, 489.
[27] Finger and Kruse, *J. Amer. Chem. Soc.*, 1956, **78**, 6034; Finger and Starr, *ibid.*, 1959, **81**, 2674.
[28] Bunnett and Conner, *J. Org. Chem.*, 1958, **23**, 305.
[29] Himel and Richards, U.S.P. 2,866,801/1958.

sulphides,[30] nitriles,[31] and hence carboxylic acids and their derivatives,[32] of nitro-compounds[33] and benzoates;[34] in synthesis of cellulose esters[35] and cyclic sulphides;[36] and dehydrohalogenation of steroids and other cyclic halides by lithium chloride in dimethylformamide,[37] where presumably in this last example the very strong nucleophile—chloride ion in dimethylformamide—displaces a *cis*-toluene-*p*-sulphonate or halide in a S_N2 Walden inversion to give a *trans*-chloride, which eliminates readily, without competing S_N1 processes, in the presence of dimethylformamide [2] and non-hydrogen bonded chloride ions—both sufficiently powerful bases to neutralise hydrogen chloride and prevent its back-addition to the olefin produced. There is some evidence that eliminations in dipolar aprotic solvents are *cis*-four-centred processes.[2] Bromide ion in dimethyl sulphoxide

TABLE 5. *A typical halogen exchange reaction in dimethylformamide at* 0·0°. $[CH_3I]_0$ = 13·28[a] *c.c.*, $[LiBr]_0$ = 13·75 *c.c.* (*Concentrations in c.c. of* 0·0200N-$AgNO_3$ *for* 6·81 *c.c. sample. Rate constants,* k_2, *in l. mole*$^{-1}$ *sec.*$^{-1}$.)

t (min.)	$[I^-]$	$[I^- + Br^-]$	$10k_2$	*t* (min.)	$[I^-]$	$[I^- + Br^-]$	$10k_2$	*t* (min.)	$[I^-]$	$[I^- + Br^-]$	$10k_2$
0·0	4·00	13·70	—	2·0	6·80	13·70	1·17	8·0	8·95	13·76	0·75
0·5	4·67	13·68	0·96	3·0	7·30	13·82	0·99	120	9·80	13·75	—
1·0	5·40	13·70	0·99	4·0	7·75	13·71	0·91	180	9·82	13·79	—
1·5	6·15	13·72	1·10	6·0	8·62	13·82	0·86				

Mean k_2 over first 30—50% reaction = 1·05 × 10^{-1} l. mole^{-1} sec.$^{-1}$; equilibrium constant K = 8·48. A duplicate estimation, $[CH_3I]_0$ = 15·00 c.c., $[LiBr]_0$ = 15·00 c.c., gave k_2 = 1·07 × 10^{-1}, K = 8·5.
[a] $[CH_3I]$ initially, and at equilibrium, estimated by warming a sample with excess of LiCl in dimethylformamide and titrating iodide ion.

should be even better for this reaction, despite the solvolyzing properties of dimethyl sulphoxide, but this remains to be tested.

Dipolar aprotic solvents are, of course, useful media for the more obvious alkyl or aryl halogen (etc.) interconversions shown in Part I [1] and this paper. The specific solvent effects in the alkylation of enol anions discussed at length by Zaugg, Horron, and Borgwardt [38] can be given an additional explanation by the postulate.

TABLE 6. *Decomposition of trimethylsulphonium bromide in dimethylformamide at* 59·8° *at ionic strength* 0·08M. $[Me_3S^+ClO_4^-]_0$ = 13·62 *c.c.*, $[LiBr]_0$ = 13·62 *c.c.* (*Concentrations in c.c. of* 0·0200N-$AgNO_3$ *for* 6·81 *c.c. sample. Run in sealed tubes. Rate constants* k_2, *in l. mole*$^{-1}$ *sec.*$^{-1}$.)

t (hr.)	$[Br^-]$	10^3k_2	*t* (hr.)	$[Br^-]$	10^3k_2	*t* (hr.)	$[Br^-]$	10^3k_2
0·00	13·30	—	2·70	8·97	1·24	24·25	4·45	0·60
0·50	12·04	1·30	2·70	9·00	1·23	24·25	4·45	0·60
1·00	11·10	1·35	4·25	7·65	1·22	36·00	4·00	—

Mean k_2 = 1·25 × 10^{-3} l. mole^{-1} sec.$^{-1}$.

Provided reactants are soluble (dimethyl sulphoxide is often the best solvent), the examples quoted and many other reactions (*e.g.*, S_N2 displacements at elements other than carbon) should be equally rapid in other dipolar aprotic solvents besides those already

[30] Carbon, *J. Amer. Chem. Soc.*, 1958, **80**, 6083.
[31] Copelin, U.S.P. 2,715,137/1955; Gahana, Schmidt, and Shah, *J. Org. Chem.*, 1959, **24**, 557; Newman and Otsuka, *ibid.*, 1958, **23**, 797; Smiley and Arnold, *ibid.*, 1960, **25**, 257; Friedman and Schechter, *ibid.*, 1960, **25**, 877.
[32] Hammond and Cram, "Organic Chemistry," McGraw-Hill, New York, 1959, p. 222.
[33] Kornblum and Powers, *J. Org. Chem.*, 1957, **22**, 455; Kornblum and Blackwood, *Org. Synth.*, 1957, **37**, 44; White and Considine, *J. Amer. Chem. Soc.*, 1958, **80**, 626; Fusco and Rossi, *Chem. and Ind.*, 1957, 1650; Belshaw, Howard, and Irving, U.S.P. 2,587,093/1952.
[34] Reist, Goodman, and Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 5775.
[35] Blume, U.S.P. 2,705,710/1955.
[36] *Org. Synth.*, 1956, **36**, 89.
[37] Hoylsz, *J. Amer. Chem. Soc.*, 1953, **75**, 4432; *Org. Synth.*, 1958, **38**, 8; Chamberlin, Tristram, Utne, and Chemerda, *J. Amer. Chem. Soc.*, 1957, **79**, 456; Pederson, Johnson, Hoylsz, and Ott, *ibid.*, 1957, **79**, 1115; Hirschmann and Miller, U.S.P. 2,837,541/1958.
[38] Zaugg, Horron, and Borgwardt, *J. Amer. Chem. Soc.*, 1960, **82**, 2895, 2905.

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reported. *Traces* of water (<0·2%) in dipolar aprotic solvents do not appear to affect rates of reaction.[1,39] The reactions are very sensitive to acid. Commercial nitrile and amide solvents contain traces of organic acids and, unless neutralized by lime and distillation, are apt to behave as protic solvents. Rates in commercial benzonitrile for the *p*-fluoronitrobenzene–azide ion reaction were immeasurably slow at 25°. Dimethyl-formamide and -acetamide should be freed by pumping from volatile, nucleophilic amines. Tetraalkylammonium salts seem to be the most soluble in dipolar aprotic solvents and thus the best source of nucleophiles.

Experimental

Materials.—Solvents, substrates, and salts of nucleophiles were prepared and/or purified by methods already described [1,4] or by recrystallization and drying. All reactants were analysed and were >99% pure. Solvents were neutral and contained no halogen or halogenoid ions, and amide solvents gave no deep yellow colour in a spot test for amines with 2,4-dinitro-1-fluorobenzene. Different batches of solvent gave identical rate constants.

Tetraethylammonium azide, sodium picrate, lithium chloride, lithium bromide, sodium azide, and sodium cyanide showed 100% purity after being heated at 100° for 3 hr. in all solvents studied. Methyl iodide was very slowly solvolysed by amide solvents and methanol (Tables 1, 7, and 8). Trimethylsulphonium perchlorate was unchanged in dimethylformamide at 59·8° after 24 hr.

Kinetics.—The technique has been described.[1,3,4] Reactions were quenched by pouring

Table 7. *A typical S_N2 reaction of methyl iodide in methanol accompanied by methanolysis at 59·8°. (Data for the reaction between sodium picrate and methyl iodide in methanol and for the methanolysis of methyl iodide measured simultaneously in methanol containing* 0·038M-$LiClO_4$. $[CH_3I]_0 = 13·07$ *c.c.*, $[NaPic]_0 = 13·07$ *c.c. Concentrations expressed in c.c. of* 0·0200N-$AgNO_3$ *for* 6·81 *c.c. sample. Rate constants, k_2, in l. mole^{-1} sec.$^{-1}$ and k_1 in sec.$^{-1}$.)*

S_N2 Substitution				Methanolysis			
t (hr.)	[I$^-$], obs.	[I$^-$], corr.	10^5k_2	*t* (hr.)	[I$^-$]	[H$^+$]	10^7k_1
0·0	0·05	0·00	—	0·0	0·05	0·00	—
1·7	0·15	0·05	—	1·7	0·10	0·05	—
22·0	1·10	0·70	1·04	22·0	0·40	0·40	3·9
72·5	2·75	2·00	1·82	72·5	0·75	0·75	2·3
93·0	3·37	2·56	1·90	93·0	0·81	0·80	2·0
165·0	4·17	3·27	1·50	165·0	0·90	0·92	1·3
237·0	5·88	4·83	1·80	237·0	1·05	1·05	1·0
Mean $k_2 = 1·8 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$.				$k_1 = 2 \times 10^{-7}$ sec.$^{-1}$; k_1 in methanol without $LiClO_4 = 1·8 \times 10^{-7}$ sec.$^{-1}$.			

Table 8. *Solvolysis of methyl iodide in* 10% *dioxan–formamide and* N*-methylformamide at* 25°. *(Concentrations in* c.c. *of* 0·0200N-$AgNO_3$ *for* 5·0 *c.c. sample. Rate constants, k_1, in sec.$^{-1}$.*

10% Dioxan–formamide. $[CH_3I]_0 = 12·60$ c.c.						*N*-Methylformamide. $[CH_3I]_0 = 13·50$ c.c.					
t (hr.)	[I$^-$]	10^6k_1	*t* (hr.)	[I$^-$]	10^6k_1	*t* (hr.)	[I$^-$]	10^6k_1	*t* (hr.)	[I$^-$]	10^6k_1
0·0	0·25	—	28·20	1·25	0·814	0·00	0·35	—	28·20	1·66	0·960
2·25	0·40	1·47	53·25	1·86	0·732	2·25	0·55	1·60	53·25	2·55	0·915
5·00	0·59	1·52	166·0	4·10	0·659	5·00	0·75	1·58	166·0	5·35	0·844
22·00	1·02	0·797	166·0	4·10	0·659	22·00	1·55	1·13	166·0	5·40	0·850

into ice-water, and halogenoids were titrated immediately with silver nitrate in the presence of barium nitrate. Typical runs are in Tables 5—8. Miscellaneous results are collected in Table 9.

[39] Cavell and Speed, *J.*, 1960, 1453.

TABLE 9. *Miscellaneous rate constants for some S_N2 reactions.* (*Initial concentrations of reactants* = 0·03—0·05M.)

CH_3I + Na Picrate in methanol at 25·1°	$k_2 = 6 \times 10^{-7}$ l. mole^{-1} sec.$^{-1}$
CH_3I + Na Picrate in D.M.F. at 25·1°	$k_2 = 3{\cdot}35 \times 10^{-5}$,, ,,
CH_3I + KSCN in methanol at 25·1°	$k_2 = 5{\cdot}26 \times 10^{-4}$,, ,,
CH_3I + NaN_3 in methanol at 25·1°	$k_2 = 7{\cdot}80 \times 10^{-5}$,, ,,
CH_3I + NaCl in methanol at 25·1°	$k_2 = 3{\cdot}0 \times 10^{-6}$,, ,,
CH_3I solvolysis by NMe_2·CHO at 100·0°	$k_1 = 2{\cdot}35 \times 10^{-5}$ sec.$^{-1}$
CH_3I solvolysis by NMe_2·COMe at 100·0°	$k_1 = 2{\cdot}0 \times 10^{-5}$,,

Reaction Products.—Methyl iodide–halogen (etc.) exchanges were substitutions, since total halogen was constant and no acid was formed. Each ion had a characteristic potential at the end-point of a silver-ion titration and was identified in this way.

Trimethylsulphonium bromide in dimethylformamide decomposed to dimethyl sulphide (identified by the mercuric chloride complex [7]), and bromide-ion consumption followed second-order kinetics, suggesting that methyl bromide was the other product.

I thank Professor J. Miller, who initiated the present series of papers and has maintained his interest and support, and Professors Sir Christopher Ingold and E. D. Hughes, and Dr. D. V. Banthorpe, for many helpful discussions.

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256. *Tautomeric Forms of Streptomycin.*

By DONALD P. YOUNG.

The salts, presumed to be of a tautomeric form of streptomycin, prepared by Heuser, Dolliver, and Stiller [1] are designated β-streptomycin salts. It is now shown that their difference from ordinary or α-streptomycin salts is a labile, chemical one. The β-streptomycin cation can exist in solution for a limited time, and the various β-salts are interconvertible by metathesis; but they revert completely to the α-form when their solutions are kept. This change can be followed polarimetrically. The only known way of forming β-streptomycin is by keeping (" ageing ") the 4-ethyl-1-3′-ethylpentyloctyl sulphate (tergitate), or a closely related salt, in the solid state. The α ⇌ β changes in both directions are accelerated by bases, and retarded by acids. β-Streptomycin tergitate reacts with carbonyl reagents much more slowly than the α-form; hence it is thought that in β-streptomycin the aldehyde group is bound by cyclisation, possibly with the methylamino-group. β-Streptomycin salts are characteristically crystalline, but they are probably all solvated in that state.

HEUSER, DOLLIVER, and STILLER [1] prepared a series of streptomycin salts which they thought to be tautomeric with the normal salts. Their supposition now appears to be correct; it is therefore proposed to designate compounds obtained by their method as β-streptomycin salts, using α-streptomycin to denote the " ordinary " form of the antibiotic.

Heuser *et al.* precipitated streptomycin as the tergitate (4-ethyl-1-3′-ethylpentyloctyl sulphate; Tergitol-7 is the sodium salt). This when kept for a few days (" aged ") became crystalline. It could then be converted into a sulphate, hydrochloride, etc., which unlike the corresponding α-streptomycin salts were crystalline. The most striking difference was shown by β-streptomycin sulphate, which was very sparingly soluble in water, whereas the α-sulphate is amorphous and extremely soluble. Formation of the β-sulphate in this way has been used commercially as a means of purifying the antibiotic. Heuser *et al.*

[1] Heuser, Dolliver, and Stiller, *J. Amer. Chem. Soc.*, 1953, **75**, 4013.

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showed that their β-streptomycin salts further differed from the α-salts in distribution coefficient and the shape of the polarogram. By making use of these they demonstrated, in a roughly quantitative manner, that β-streptomycin salts reverted to the α-form in solution, and that this change was retarded by the presence of acids.

The clearest evidence [2] that the phenomenon was not merely one of allotropy or solvation is that solutions of β-streptomycin hydrochloride gave a precipitate of the β-sulphate on addition of sulphate ion, so that the β-streptomycin cation preserved its identity in solution.

The observations of Heuser *et al.* have now been confirmed and extended. β-Streptomycin hydrochloride was converted, by precipitation of its freshly made aqueous solution with the appropriate sodium salt, into the biphenyl-4-sulphonate, 5-cyclohexyl-2-hydroxy-3-methylbenzoate, and 2-hydroxy-5-isobutyl-3-methylbenzoate. In the case of the first two of these, the α-streptomycin salts are also crystalline,[3,4] but the pairs of salts had

FIG. 1. *Mutarotation of β-streptomycin tergitate (c, 5).*

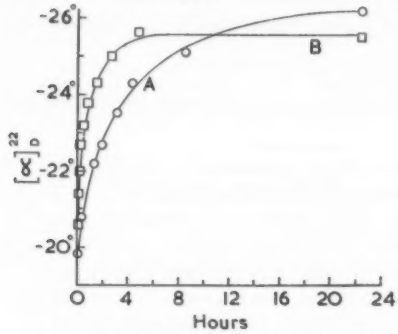
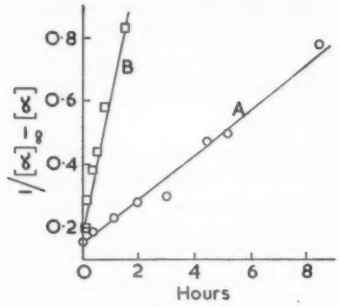


FIG. 2. *Second-order plot for mutarotation of β-streptomycin tergitate.*



(A) *In neutral methanol.* (B) *In* 0·01N-*methanolic sodium hydroxide.*

different *X*-ray diffraction patterns. These three new salts were then converted into β-streptomycin sulphate.

The reversion of β- to α-streptomycin salts in solution can be followed polarimetrically, most easily with the tergitate in methanol (50 mg./ml.), which showed a change of $[\alpha]_D^{20}$ from −19·8° to −26·4°. As ordinarily prepared, the β-tergitate reverted in this way to the α-form in a few days. In 0·01N-methanolic sodium hydroxide, the mutarotation was more rapid (Fig. 1); but in 0·01N-methanolic sulphuric acid there was no measurable alteration in $[\alpha]_D$ during 18 hr., and in 0·1N-methanolic acetic acid a change of only 0·2° in 24 hr., corresponding to *ca.* 3% conversion into the α-form. Further, if the β-tergitate was recrystallised from methanol–water containing a trace of sulphuric acid, it became stable in methanol solution, and its stability was not destroyed by subsequent recrystallisation from unacidified methanol. The "stabilised" tergitate did nevertheless revert rapidly to the α-form if a trace of sodium hydroxide was added to its solution. The change, surprisingly, was of the second order in all cases.

β-Streptomycin 5-cyclohexyl-2-hydroxy-3-methylbenzoate showed a similar, very rapid change in rotation in methanol solution as it reverted to the α-form. For the hydrochloride in aqueous solution the change was too small and too fast for accurate observation: $[\alpha]_D^{22}$ was −82·3° ten minutes after preparation (50 mg./ml.), falling to a final value of −79·1° (24 hr.) (at least three-quarters complete in 50 min.). Gravimetric estimation of the β-tautomer by precipitation as sulphate led to the same conclusion. The change

[2] Heuser, U.S.P. 2,663,464.
[3] Ziegler, U.S.P. 2,857,376.
[4] Ziegler, U.S.P. 2,857,375.

was appreciably retarded by 0·001N-concentration of hydrochloric acid, and in 0·01N-acid it occupied many hours; here again the reaction was approximately of the second-order (Fig. 3); the rate, however, varied with different batches of β-salt. In 5% aqueous toluene-*p*-sulphonic acid, the β-hydrochloride initially showed $[\alpha]_D^{18}$ −70·8° changing, in the opposite sense, to −78·5° (final: 24 hr.).

Probably all crystalline β-streptomycin salts are solvated. The sulphate lost the equivalent of $7H_2O$ when dried; the dried salt dissolved in water, but the crystalline hydrate was soon precipitated. *X*-Ray examination of the dried material revealed a partly orientated structure. The hydrochloride crystallised from methanol with 2 mol. of methanol, which was readily driven off, leaving an amorphous substance. Recrystallised β-streptomycin tergitate is hydrated.[1]

The "ageing" of streptomycin tergitate involves a spontaneous change from the α- to the β-form, accompanied by crystallisation. Precipitated α-streptomycin tergitate is soap-like and difficult to purify, but samples were conveniently obtained by keeping a methanolic solution of the β-tergitate for a few days and then removing the solvent. This left the α-tergitate as a glass, stable when dry. Only in presence of water did it change into the β-form. Like the β ⟶ α change, this was strongly accelerated by a trace of alkali, and inhibited by aqueous acid.

So far, no other streptomycin salt except the related 4-ethyl-1-isobutyloctyl sulphate [2] (from Tergitol-4) has been found which changes from the α- into the β-form. In all streptomycin salts examined, there was no detectable amount of β-form in equilibrium with the α-tautomer in solution; solutions of α-streptomycin showed no measurable mutarotation, and it has proved impossible to obtain the β-sulphate from them by adding sulphate ion. It is therefore clear that a change towards the β-form could not occur in a solid phase in contact with a solvent containing appreciable amounts of dissolved streptomycin. Although the presence of water is necessary for the formation of β-streptomycin tergitate—presumably because the driving force is crystallisation of the hydrate—the tergitate is very insoluble in water; this combination of properties may be almost unique amongst streptomycin salts. Heuser *et al.*[1] thought that some α-tergitate was present at equilibrium, which may indeed arise from back-reaction in the aqueous phase.

It has been established that the β-streptomycin cation has an independent existence, and that its salts have the same composition as the corresponding α-streptomycin ones. The equilibrium between the two is sufficiently mobile to justify the term tautomerism, although, in the absence of molecular-weight determinations, reversible dimerisation cannot be excluded.

Mannosidostreptomycin shows the same phenomenon,[2] but dihydrostreptomycin and streptomycin oxime do not, which implicates the aldehyde group as the seat of the tautomerism. This was confirmed when it was found that β-streptomycin tergitate, in a metastable condition in methanolic 0·1N-acetic acid, reacted much more slowly than the α-salt with hydroxylamine and 4-phenylsemicarbazide (reactions followed polarimetrically) (cf. Fig. 4). Evidently, in β-streptomycin the aldehyde group is combined in such a way that it has become unreactive.

Heuser *et al.*[1] interpreted their polarographic results (which we have confirmed) in the opposite sense, namely, that it was the α-tautomer that had a bound (unreactive) aldehyde group. The extra polarographic wave on the more positive side with the α-form could, however, equally be interpreted as arising from an easily reducible group, *i.e.*, a free aldehyde group, in that tautomer.

The pronounced effect of bases on the α ⇌ β changes is manifested at the neutralisation point of the third basicity of the streptomycin cation. This suggests that the weakest basic group, *i.e.*, the NHMe-group, may also be concerned in the tautomerism. Possibly it combines with the aldehyde group to form a ·CH(OH)·NMe· structure; this would result in a 7-membered ring, which, from atomic models, is sterically possible (dimerisation of the type common amongst α-ketols is sterically unlikely). The fact that the β ⟶ α

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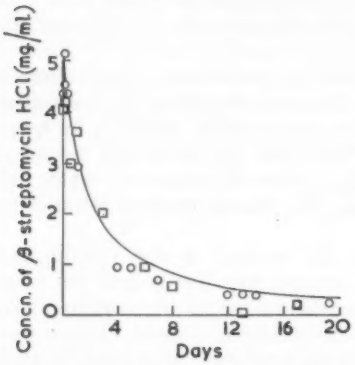
reaction, resulting in the freeing of a bound aldehyde group, is of the second order is puzzling, but it need not indicate that the reaction is bimolecular. There is no appreciable difference in base-strength between α- and β-streptomycin.

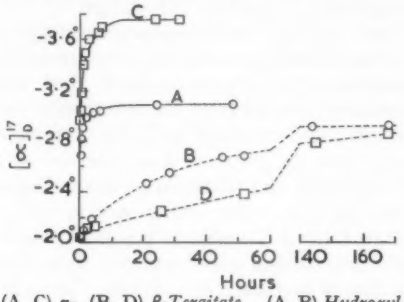
Other authors [5] have obtained evidence, from polarographic and distribution experiments, of tautomerism of streptomycin in solution. Their results might at first sight be explained by an equilibrium between α- and β-streptomycin. However, it now appears that this equilibrium would be entirely on the side of the α-form; thus there may be more than two desmotropic forms of streptomycin.

FIG. 3. *Change of β- into α-streptomycin hydrochloride in* 0·01N-*hydrochloric acid at* 17°.



○ *Polarimetric observations.* □ *Gravimetric observations.* —— *Calculated second-order curve,* $k = 0{\cdot}0125$ g. ml.$^{-1}$ day^{-1}.

FIG. 4. *Reaction of streptomycin tergitates* (0·6 *mmole) with carbonyl reagents in* 0·1N-*acetic acid in methanol* (20 ml.).



(A, C) α-, (B, D) β-*Tergitate.* (A, B) *Hydroxylamine acetate* (0·7 mmole); (C, D) *4-phenylsemicarbazide* (0·6 mmole).

EXPERIMENTAL

Samples for analysis and bioassay were dried at 60°/0·1 mm. for 8 hr.; this did not always completely remove water. Nitrogen analyses, whether by the Dumas or the Kjeldahl method, often gave low results for streptomycin derivatives. Bioassays were by *Bacillus subtilis* NTCC 8236. Rotations were measured with 2-dm. tubes.

β-Streptomycin tergitate, m. p. 155—158°, was prepared by precipitation, "ageing," and recrystallisation, as described by Heuser *et al.*[1] Under the polarising microscope it appeared as small flat birefringent needles.

Change of β- into α Streptomycin Tergitate.—A solution of β-tergitate in methanol was kept until the rotation ceased to rise. The apparent pH of the solution remained unchanged (within 0·1 unit). Evaporation under a vacuum left the α-tergitate as a glass, soluble in carbon tetrachloride and acetone in which the β-tergitate is insoluble; such solutions did not crystallise, even with added water. With aqueous guanidine sulphate and butanol it gave no crystalline streptomycin sulphate.

Evaporation of a solution of β-tergitate in 0·01N-methanolic sulphuric acid after 18 hr. left unchanged β-tergitate, which crystallised. This was convertible into β-streptomycin sulphate.

Conversion of α- into β-Streptomycin Tergitate.—(a) *Under neutral conditions.* α-Streptomycin tergitate, obtained as above, remained unchanged for months in a closed vessel. When covered with distilled water, the glass softened to a jelly, then after 3 days became friable and opaque. After 7 days it was dried, and then consisted of birefringent crystals, m. p. 149°. In methanol $[\alpha]_D$ changed from −19·9° to −24·1°. By evaporation of this solution and addition of water, the cycle could be repeated.

(b) *In presence of alkali.* α-Streptomycin tergitate was covered with 0·01N-aqueous sodium

[5] Bricker and Vail, *J. Amer. Chem. Soc.*, 1951, **73**, 585; Titus and Fried, *J. Biol. Chem.*, 1948, **174**, 57.

hydroxide. In ½ hr. it had peptised to a thick colloidal suspension, but after 1 hr. this coagulated to waxy masses, leaving a mobile supernatant liquid. The solid was crystalline, with m. p. ~155°.

(c) *Under acid conditions.* The α-tergitate, after 10 days under 0·01N-hydrochloric acid, was unchanged.

" Stabilised " β-Streptomycin Tergitate.—Crude β-tergitate (15 g.) was dissolved in methanol (100 ml.) containing sulphuric acid (0·02 ml.) at 30—40°. The solution was cooled and water (10 ml.) added. After some hours at 0° the crystals (11·2 g.) were collected and recrystallised from methanol–water. They then had m. p. 145°, $[\alpha]_D^{28}$ −21·6° in methanol, rising to −22·6° after 12 days.

Reaction of Streptomycin Tergitates with Hydroxylamine.—To streptomycin tergitate (1 g.) in 0·1N-methanolic acetic acid (20 ml.) was added a solution (1 ml.) of hydroxylamine acetate [from hydroxylamine hydrochloride (1·02 g.) and sodium acetate (1·25 g.) in methanol, filtered, and made up to 25 ml.].

When the reaction with the α-tergitate was complete (48 hr.; Fig. 4), 0·9N-aqueous methylamine sulphate (2·2 ml.) was added, and the precipitated *oxime sulphate* (0·38 g.) was collected (Found: C, 32·9; H, 6·4; N, 14·2; S, 6·8. $C_{21}H_{40}N_8O_{12},1\frac{1}{2}H_2SO_4,3H_2O$ requires C, 32·9; H, 6·2; N, 14·1; S, 6·1%). This was biologically almost inactive (potency found, 28 u./mg.).

The reaction with β-tergitate was not complete after 7 days. The product at that point was converted into sulphate, which from its assay (80 u./mg.) was oxime containing an appreciable amount of unchanged streptomycin.

Streptomycin Oxime Tergitate.—To a solution of α-streptomycin sulphate (7·3 g.) and hydroxylamine hydrochloride (1·04 g.) in water (50 ml.), sodium hydroxide was added as necessary to keep the pH at 6. After 3 hr., a slight excess of Tergitol-7 was added. The pasty precipitate was centrifuged off and washed with water. It did not crystallise and was dried to a glass (Found: C, 53·8; H, 9·1; N, 6·4; S, 6·0. $C_{21}H_{40}N_8O_{12},3C_{17}H_{26}O_4S,2H_2O$ requires C, 53·1; H, 8·8; N, 6·9; S, 5·9%). With methylamine sulphate in aqueous methanol, it gave the oxime sulphate (potency 48 u./mg.).

Reaction of Streptomycin Tergitates with 4-Phenylsemicarbazide.—Streptomycin tergitate (1·0 g.) and 4-phenylsemicarbazide (0·10 g.) were dissolved in 0·1N-methanolic acetic acid (total volume, 20 ml.).

The reaction with α-tergitate was complete in 24 hr. (Fig. 4). 0·9N-Aqueous methylamine sulphate (2·2 ml.) was added to this solution to precipitate *streptomycin 4-phenylsemicarbazone sulphate*, which was washed with methanol and dried. It was biologically inactive (Found: potency, 20 u./mg.; C, 36·7; H, 6·2; N, 14·0; S, 5·3. $C_{28}H_{46}N_{10}O_{12},1\frac{1}{2}H_2SO_4,3H_2O$ requires C, 36·7; H, 6·1; N, 15·3; S, 5·3%). The reaction with β-tergitate was still incomplete (cf. Fig. 4) after 4 weeks, when the $[\alpha]_D^{17}$ had reached −35·4°.

β-Streptomycin Hydrochloride.—The hydrochloride, prepared in methanol [1] and air-dried, formed birefringent rhombic prisms. On drying at 60°/0·1 mm. for 8 hr., it lost 9% in weight (corresponding to 2MeOH) and became amorphous, although still apparently retaining water (Found: C, 34·8, 35·2; H, 6·7, 6·4; Cl, 15·0, 15·2; N, 13·4, 13·8%; potency, 861 u./mg. Calc. for $C_{21}H_{39}N_7O_{12},3HCl,H_2O$: C, 34·6; H, 6·2; Cl, 15·0; N, 13·8%; potency, 820 u./mg.). The methanol-free material was soluble in methanol; a 5% solution soon deposited crystals of the methanol solvate, which was almost insoluble. The crystalline compound gave a diffuse *X*-ray pattern, but it became amorphous during the exposure.

Conversion of β- into α-Streptomycin Hydrochloride (Fig. 3).—Solutions of the β-hydrochloride (50 mg./ml.) were observed polarimetrically, and the amount of β-streptomycin was estimated at intervals gravimetrically: an aliquot part was treated with an equal volume of 0·5N-guanidine sulphate (acidified to pH 3) and kept at 0° for 30 min. The precipitated β-sulphate was filtered off (filter-stick), washed with 0·1N-sulphuric acid, ethanol, and acetone, briefly dried *in vacuo*, and weighed.

β-Streptomycin Tergitate from β-Hydrochloride.—A fresh solution of the β-hydrochloride in water with a trace of hydrochloric acid was treated with Tergitol-7. The tergitate was precipitated immediately in crystalline condition (m. p. 148—149°).

β-Streptomycin Biphenyl-4-sulphonate.—A hot solution of sodium biphenyl-4-sulphonate (1·90 g.) in water (50 ml.) was added to a freshly prepared one of the β-hydrochloride (1·60 g.) in water (50 ml.). The *β-streptomycin salt* was precipitated immediately (yield 68%); it had m. p. 187—189° (decomp.) (Found: C, 51·4; H, 5·7; N, 7·5; S, 7·5. $C_{21}H_{39}N_7O_{12},3C_{12}H_{10}O_3S,3H_2O$ requires

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C, 51·1; H, 5·6; N, 7·3; S, 7·2%). With the equivalent amount of guanidine sulphate in aqueous methanol, it gave β-streptomycin sulphate (92%), which was crystallised from water; its identity was checked by its infrared spectrum.

In a similar manner were prepared *β-streptomycin 5-cyclohexyl-2-hydroxy-3-methylbenzoate* (85%), m. p. 170—175° (decomp.; rapid heating), $[\alpha]_D^{19}$ −22·0° (5 min.), −26·7° (190 min.), −27·0° (27½ hr.) in MeOH (*c* 5) (Found: C, 57·9, 57·6; H, 7·7, 7·6; N, 7·2, 7·2. $C_{21}H_{39}N_7O_{12},3C_{14}H_{18}O_3$ requires C, 57·7; H, 7·3; N, 7·6%), and the *2-hydroxy-5-isobutyl-3-methylbenzoate* (83%), m. p. 90—95° (Found: C, 55·2; H, 7·4; N, 7·5%; potency, 437 u./mg. $C_{21}H_{39}N_7O_{12},3C_{12}H_{16}O_3,2H_2O$ requires C, 55·1; H, 7·4; N, 7·9%; potency, 469 u./mg.). Both these were converted in good yield into β-streptomycin sulphate.

From α-streptomycin sulphate were obtained α-streptomycin biphenyl-4-sulphonate [3] (85%), m. p. 187·5—189° (charred) (Found: C, 50·2; H, 5·5; N, 6·6; S, 7·4%: potency, 466, 453 u./mg. Calc. for $C_{21}H_{39}N_7O_{12},3C_{12}H_{10}O_3S,4H_2O$: C, 50·4; H, 5·8; N, 7·2; S, 7·1%; potency, 432 u./mg.), and 5-cyclohexyl-2-hydroxy-3-methylbenzoate [4] (99%), m. p. 160—165° (charred), 93° (decomp.; in preheated bath), $[\alpha]_D^{21}$ −27·4° in MeOH (*c* 5) (Found: C, 55·6; H, 7·7; N, 6·3%; potency, 448, 510 u./mg. Calc. for $C_{21}H_{39}N_7O_{12},3C_{14}H_{18}O_3,2H_2O$: C, 56·1; H, 7·4; N, 7·4%; potency, 441 u./mg.). The *X*-ray patterns of these two were similar to, but distinguishable from, those of the corresponding β-salts. α-Streptomycin hydroxyisobutylmethylbenzoate formed a gum.

β-Streptomycin Sulphate from Hydrochloride.—β-Streptomycin hydrochloride (5·0 g.) was dissolved in water (100 ml.), and 0·9N-methylamine sulphate (25 ml.) immediately added. The β-sulphate that crystallised was filtered off, washed with a little water and then with ethanol, and air-dried (2·9 g.). When dried at 60°/0·1 mm. for 8 hr., this product lost 15% in weight (corresponding to $7H_2O$), and was then anhydrous (Found: C, 34·8; H, 6·1; N, 12·7; S, 6·2%; potency, 817 u./mg. Calc. for $C_{21}H_{39}N_7O_{12},1\frac{1}{2}H_2SO_4$: C, 34·6; H, 5·8; N, 13·5; S, 6·6%; potency, 798 u./mg.). It then dissolved in water, but the solution rapidly afforded crystals of the hydrate. This recrystallised from 0·01N-sulphuric acid (dissolution at 40°) at 0°. The hydrate gave a sharp *X*-ray pattern; the dried β-sulphate gave diffuse rings, suggesting that part of the crystalline orientation remained. The infrared spectrum (KBr disc) was indistinguishable from that of α-streptomycin sulphate, in which no C=O band is detectable.

Thanks are expressed to Dr. C. C. F. Blake for *X*-ray powder diagrams, to Mr. A. R. Philpotts for infrared spectra, to Mr. R. J. Thompson for polarography, and to Dr. R. H. Hall for his interest.

The Distillers Company Limited, Research and Development Department, Great Burgh, Epsom, Surrey. [*Received, September 1st*, 1960.]

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257. *Aliphatic Friedel–Crafts Reactions. Part III.*[1] *The Acylation of Cycloheptene and Cyclo-octene.*

By N. Jones, H. T. Taylor, and (in part) E. Rudd.

Cycloheptene and cyclo-octene are readily acylated with acid chloride–aluminium chloride complex in methylene chloride to provide, after distillation from sodium carbonate, an unsaturated ketone. The initial stages of Braude and Coles's azulene synthesis have been shortened.

This paper is one of a series on the preparative usefulness of the acetylation of olefins by the Friedel–Crafts method. The reaction has been less studied than the corresponding acylation of aromatic compounds. In every case, reactions do not proceed so clearly, the essential difference being the fate of the hydrogen chloride. Direct yields of chloride (I) or unsaturated ketone (II) depend mainly on the temperature, an increase favouring the olefin but at the expense of reduced overall yields (owing to polymerisation). The unsaturated product can be obtained (if not formed directly) by dehydrohalogenation of

[1] Part II, Jones and Taylor, *J.*, 1959, 4017.

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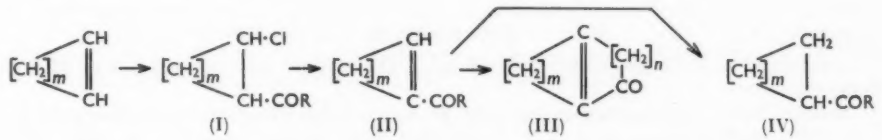
the chloride with anhydrous sodium carbonate.[2] Preliminary calorimetric work shows that polymerisation of cycloheptene and cyclo-octene occurs more readily than of cyclohexene in the presence of aluminium chloride, and lower reaction temperatures for the acylation are preferable.



Cycloheptene and cyclo-octene have now been acylated with a variety of acyl halides, slightly lower yields being obtained (owing to polymerisation) than from cyclopentene [1] and cyclohexene.[3] Experimental technique was similar to that previously described. Friess and Pinson,[4] using the rather drastic conditions of Nenitzescu and Goranescu,[5] obtained only a mixture of 3- and 4-methylcyclohexane on attempted acetylation of cycloheptene: at lower temperatures, however, acetylcycloheptene was obtained when carbon disulphide was used as solvent.[6,7] Cycloheptene and cyclo-octene readily react with an acyl chloride–aluminium chloride complex in methylene chloride at −15° (in the case of the less reactive benzoyl chloride at 10—15°, and β-naphthoyl chloride did not react at 40°) to provide, after distillation from anhydrous sodium carbonate, the cycloalkenone (II). Most of these compounds have been quantitatively hydrogenated to the saturated ketones (IV).

Interaction of β-chloropropionyl chloride and cycloheptene, though prevented by the incursion of polymerisation from affording cycloheptenyl vinyl ketone, provides a product which, on treatment with 98% formic acid and phosphoric acid,[8] affords bicyclo[5,3,0]dec-1(7)-en-8-one [9,10] (III; $m = 5$, $n = 2$) shortening the initial stages of Braude and Coles's

Interaction of cycloalkenes with acylating agents at −15° unless otherwise stated.

Reactants		Product	Yield (%)
Cycloheptene	AcCl	C_7H_{11}·COMe	70
,, ...	Et·COCl	C_7H_{11}·COEt	58
,, ...	Pr^n·COCl —	C_7H_{11}·COPr^n	45
,, ...	$MeO_2C·[CH_2]_2·COCl$ [a]	C_7H_{11}·CO·$[CH_2]_2·CO_2Me$	26
,, ...	BzCl [a]	C_7H_{11}·COPh	50
,, ...	β-$C_{10}H_7$·COCl [b]	—	0
,, ...	Cl·$[CH_2]_2$·COCl	C_7H_{11}·CO·$[CH_2]_2$·Cl	60
,, ...	Cl·$[CH_2]_3$·COCl	C_7H_{11}·CO·$[CH_2]_3$·Cl	54
Cyclo-octene	AcCl	C_8H_{13}·COMe	48
,, ...	BzCl	C_8H_{13}·COPh	33

[a] At 10°. [b] At 40°. [c] At 15°.

azulene synthesis.[10] Attempted cyclisation of the product of interaction of cycloheptene and γ-chlorobutyryl chloride to provide bicyclo[5,4,0]undec-1(7)-en-8-one (III; $m = 5$, $n = 3$) resulted in polymerisation.

Cyclo-octene has been acetylated by Ruzicka and Boekenoogen,[11] using Darzens's method,[12] and they prepared the semicarbazone, m. p. 180°, of the reduced product,

[2] Christ and Fuson, *J. Amer. Chem. Soc.*, 1937, **59**, 893.
[3] Baddeley, Taylor, and Pickles, *J.*, 1953, 124.
[4] Friess and Pinson, *J. Amer. Chem. Soc.*, 1951, **73**, 3512.
[5] Nenitzescu and Goranescu, *Ber.*, 1936, **69**, 1820.
[6] Tamb and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1952, **74**, 2117.
[7] Rosenhelder and Guisberg, *J.*, 1954, 2955.
[8] Nazarov and Burmistrova, *Bull. Acad. Sci. U.S.S.R.*, 1947, 51.
[9] Islam and Raphael, *J.*, 1953, 2247.
[10] Braude and Coles, *Nature*, 1951, **168**, 879; *J.*, 1953, 2208.
[11] Ruzicka and Boekenoogen, *Helv. Chim. Acta*, 1931, **14**, 1319.
[12] Darzens, *Compt. rend.*, 1910, **150**, 707; **151**, 758.

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cyclo-octyl methyl ketone. Reppe *et al.*[13] record the m. p. of the semicarbazone of cyclo-octenyl methyl ketone as 211°; we record the m. p. as 160° after repeated recrystallisation from ethanol, and agree with the m. p. of the derivative recorded by Ruzicka *et al.*

Our various results are summarised in the Table.

Experimental

Reaction of Acid Chlorides with Cycloalkenes.—The method was as described in Part II (0·20-molar scale).

Acetyl chloride and cycloheptene at −10° provided cycloheptenyl methyl ketone (19·6 g.), b. p. 210° [semicarbazone, m. p. 193° (Tamb and Szmuszkovicz [6] record m. p. 194—195°); 2,4-*nitrophenylhydrazone*, m. p. 173° (Found: N, 17·8. $C_{15}H_{18}N_4O_4$ requires N, 17·6%)]. A sample (2·40 g.) absorbed hydrogen (395 ml. corr. to S.T.P. Calc. for $C_9H_{14}O$: 1 mol., 389 ml.) in the presence of palladium. The reduced product, cycloheptyl methyl ketone gave a *semicarbazone*, m. p. 162° (Found: N, 21·2. $C_{10}H_{19}N_3O$ requires H, 21·3%), and a 2,4-*dinitrophenylhydrazone*, m. p. 195° (Found: N, 17·9. $C_{15}H_{20}N_4O_4$ requires N, 17·5%).

Propionyl chloride and cycloheptene at −10° gave cycloheptenyl ethyl ketone (19·0 g.), b. p. 220°, which gave a *semicarbazone*, m. p. 163° (Found: C, 63·0; H, 9·10; N, 20·0. $C_{11}H_{19}N_3O$ requires C, 63·2; H, 9·10; N, 20·1%). A sample (2·75 g.) absorbed hydrogen (410 ml. corr. to S.T.P. $C_{10}H_{16}O$ requires 1 mol., 405 ml.) in the presence of palladium. The reduced product, cycloheptyl ethyl ketone gave a 2,4-*dinitrophenylhydrazone*, m. p. 113° (Found: C, 57·3; H, 6·5; N, 16·7. $C_{16}H_{22}N_4O_4$ requires C, 57·5; H, 6·6; N, 16·8%).

Butyryl chloride and cycloheptene at −10° gave cycloheptenyl propyl ketone (15·0 g.), b. p. 233°, which gave a 2,4-*dinitrophenylhydrazone*, m. p. 123° (Found: C, 58·8; H, 6·28; N. 16·2. $C_{17}H_{22}N_4O_4$ requires C, 59·0; H, 6·4; N, 16·2%).

2-Methoxycarbonylpropionyl chloride and cycloheptene at 15° gave methyl γ-cyclohept-1-enyl-γ-oxobutyrate (10·5 g.), b. p. 162°/15 mm., which gave a *semicarbazone*, m. p. 176° (Found: C, 58·2; H, 7·8; N, 15·9. $C_{13}H_{21}N_3O_3$ requires C, 58·4; H, 7·9; N, 15·7%).

Benzoyl chloride and cycloheptene at 10° gave benzoylcycloheptene (20 g.), b. p. 178°/18 mm., which gave a *semicarbazone*, m. p. 172° (Found: C, 69·8; H, 7·3; N, 16·0. $C_{15}H_{19}N_3O$ requires C, 70·0; H, 7·4; N, 16·3%), and a 2,4-*dinitrophenylhydrazone*, m. p. 107° (Found: C, 63·0; H, 5·4; N, 14·5. $C_{20}H_{20}N_4O_4$ requires C, 63·2; H, 5·3; N, 14·7%).

β-Naphthoyl chloride and cycloheptene did not react during 1 hr. at temperatures up to 40°.

β-Chloropropionyl chloride and cycloheptene at −10° gave a product (38 g.) before distillation from sodium carbonate (Found: Cl, 20·22. Calc. for $C_{10}H_{16}Cl_2O$: Cl, 31·8. Calc. for $C_{10}H_{15}ClO$: C, 19·0%). Distillation from anhydrous sodium carbonate afforded a fraction (23 g.), b. p. 125°/15 mm. (Found: Cl, 7·8%). (Subsequent slow redistillation from sodium carbonate, followed by fractional distillation, effected polymerisation.) The product (21 g.), together with phosphoric acid (10 g.) and 98% formic acid (30 g.) was kept at 90° for 4 hr. under nitrogen. Hydrogen chloride was evolved, and the product was poured into water and extracted with ether (2 × 50 ml.). The extract was dried (Na_2CO_3) and after solvent removal gave bicyclo-[5,3,0]dec-1(7)-en-8-one (10 g.), b. p. 120°/15 mm. [semicarbazone, m. p. 238—240° (decomp.); 2,4-dinitrophenylhydrazone m. p. 228°; Braude and Coles [10] record m. p.s 238° and 226° respectively]. A sample (2·37 g.) absorbed hydrogen (364 ml. corr. to S.T.P. Calc. for $C_{10}H_{14}O$: 1 mol., 354 ml.) in the presence of palladium. The reduced product, bicyclo[5,3,0]dec-8-one gave a *semicarbazone*, m. p. 225° (Found: C, 63·4; H, 8·9; N, 20·3. $C_{11}H_{19}N_3O$ requires C, 63·2; H, 9·1; N, 20·1%), and a 2,4-*dinitrophenylhydrazone*, m. p. 190° (Found: C, 58·1; H, 6·1; N, 16·8. $C_{16}H_{20}N_4O_4$ requires C, 57·8; H, 6·0; N, 16·9%).

γ-Chlorobutyryl chloride and cycloheptene at −10° gave a product (40 g.) before distillation from sodium carbonate (Found: Cl, 18·9. Calc. for $C_{11}H_{18}Cl_2O$: Cl, 30·0. Calc. for $C_{11}H_{17}ClO$: C, 17·7%). Distillation from anhydrous sodium carbonate gave 3-*chloropropyl cycloheptenyl ketone* (Found: Cl, 17·9. $C_{11}H_{17}ClO$ requires Cl, 17·7%). The product (25 g.), together with phosphoric acid (12 g.) and 98% formic acid (36 g.), was kept at 90° for 6 hr. under nitrogen. Isolation of the product as above gave a tar which could not be distilled.

Acetyl chloride and cyclo-octene at −15° provided cyclo-octenyl methyl ketone (14·5 g.),

[13] Reppe, Schlichling, and Westphal, U.S.P. 2,759,926/1956.

b. p. 108°/12 mm., which gave a semicarbazone, m. p. 160° (Reppe *et al.*[13] record m. p. 211°) (Found: C, 63·0; H, 9·0; N, 21·0. Calc. for $C_{11}H_{19}N_3O$: C, 63·2; H, 9·1; N, 21·1%). A sample (2·6 g.) absorbed hydrogen (376 ml. corr. to S.T.P. Calc. for $C_{10}H_{16}O$: 1 mol., 383 ml.) in the presence of palladium. The reduced product, cyclo-octyl methyl ketone, gave a semicarbazone, m. p. 180° (Ruzicka and Boerkenoogen [11] record m. p. 180°).

Benzoyl chloride and cyclo-octene at 10° provided benzoylcyclo-octene (14 g.), b. p. 168°/15 mm., that gave an *oxime*, m. p. 123° (Found: C, 78·4; H, 8·25; N, 5·95. $C_{15}H_{19}NO$ requires C, 78·6; H, 8·3; N, 6·1%), and a *2,4-dinitrophenylhydrazone*, m. p. 134° (Found: C, 63·6; H, 5·65; N, 14·5. $C_{21}H_{22}N_4O_4$ requires C, 64·0; H, 5·6; N, 14·2%).

We thank Mr. R. Muir (Courtaulds Ltd.) for a number of microanalyses.

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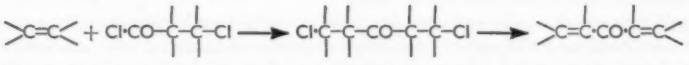
258. *Aliphatic Friedel–Crafts Reactions. Part IV.* The Preparation of Divinyl Ketones.*

By N. JONES and H. T. TAYLOR.

Ethylene or propene combines with an acyl chloride–aluminium chloride complex in methylene chloride to provide chloro-ketones, which on dehydrohalogenation afford divinyl ketones. Cyclisation of dipropenyl ketone gives 3,4-dimethylcyclopent-2-en-1-one.

THE acylation of an olefin with a β-chloro-acid chloride, through the agency of aluminium chloride, readily affords 2,2′-dichlorodialkyl ketones, which on complete dehydrohalogenation provide divinyl ketones:



Di-2-chloroethyl ketone, prepared by interaction of ethylene and β-chloropropionyl chloride,[1] when distilled from anhydrous sodium carbonate, provides divinyl ketone. Attempts to effect dehydrohalogenation by *NN*-dimethylaniline,[2] aluminium chloride, or alcoholic potassium hydroxide resulted in polymerisation. Divinyl ketone readily polymerises [3] and was identified by quantitative hydrogenation to diethyl ketone.

Reaction of ethylene with crotonoyl chloride, or of propene with β-chloropropionyl chloride, provides propenyl vinyl ketone, dehydrohalogenation taking place during the reaction if carried out at 25—30°. The formation of a divinyl ketone is readily detected by the lachrymatory properties and the odour produced. Propene and crotonoyl chloride provide dipropenyl ketone.

Propene is less reactive towards an acid chloride–aluminium chloride complex in methylene or ethylene chloride than is ethylene. Higher reaction temperatures (25—30°) are required, and the reaction is indefinite in that absorption of propene does not stop after one mol. has been absorbed.[4] n-Propyl iodide did not react with the acetyl chloride–aluminium chloride complex at 40° after one hour, but isopropyl bromide afforded the expected methyl propenyl ketone.

On treatment with phosphoric acid and 98% formic acid,[5] divinyl ketone and vinyl propenyl ketone polymerise, but dipropenyl ketone yields 3,4-dimethylcyclopent-2-en-1-one; this on hydrogenation provided 3,4-dimethylcyclopentanone.

* Part III, preceding paper.

[1] Baddeley, Taylor, and Pickles, *J.*, 1953, 124.
[2] B.P. 459,537/1937.
[3] Nazarov, numerous papers, *Bull. Acad. Sci. U.S.S.R.*, 1947 onwards.
[4] See Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Inc., New York, 1942.
[5] Nazarov and Burmistrova, *Bull. Acad. Sci. U.S.S.R.*, **1947**, 51.

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Our various results are summarised in the Table.

Interaction of olefin with acetylating agent, at 25—30° unless otherwise stated.

Reactants		Product	Yield (%)
$CH_2{:}CH_2$	$Cl{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$	$(CH_2{:}CH)_2CO$	35 [a]
,,	$CH_2{\cdot}CH{:}CH{\cdot}COCl$	$CH_2{:}CH{\cdot}CO{\cdot}CH{:}CHMe$	52
$Me{\cdot}CH{:}CH_2$	AcCl	$Me{\cdot}CH{:}CH{\cdot}COMe$ }	40
	Ac_2O	$Cl{\cdot}CHMe{\cdot}CH_2{\cdot}COMe$ }	
,,	$CH_2{\cdot}CH{:}CH{\cdot}COCl$	$(Me{\cdot}CH{:}CH)_2CO$	40
,,	$Cl{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$ [b]	$CH_2{\cdot}CH{\cdot}CO{\cdot}CH{:}CHMe$	45
,,	$MeO_2C{\cdot}[CH_2]_2{\cdot}COCl$	$Me{\cdot}CH{:}CH{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2Me$	35
Pr^nI	AcCl [c]	—	0
Pr^iBr	AcCl [c]	$MeCH{:}CH{\cdot}COMe$	43

[a] After distillation from Na_2CO_3. [b] At 35°. [c] At 40°.

Experimental

Propene and Acetyl Chloride.—Powdered aluminium chloride (0·60 mole) was added with stirring to acetyl chloride (0·50 mole) in methylene chloride (200 ml.). The acetyl chloride–aluminium chloride complex was decanted from the excess of chloride into the reaction vessel, and dry propene was passed into the stirred solution at 25—30° (no reaction occurred at 0°). A slow, steady absorption occurred, which slackened but did not cease after 12 l. had been absorbed. The mixture was poured into dilute hydrochloric acid and ice, the organic layer separated and dried (Na_2SO_4), and the solvent removed. Distillation of the residue (41 g.) gave methyl propenyl ketone (4 g.), b. p. 103°, which afforded a 2,4-*dinitrophenylhydrazone*, m. p. 156—157° (Found: N, 21·0. $C_{11}H_{12}N_4O_4$ requires N, 21·2%), and 2-chloroethyl methyl ketone (15 g.), b. p. 123—125° (Found: Cl, 29·0. Calc. for C_5H_9ClO: Cl, 29·4%), together with higher-boiling material (20 g.). Distillation of 2-chloroethyl methyl ketone from anhydrous sodium carbonate gave methyl propenyl ketone, which was hydrogenated to methyl propyl ketone (2,4-dinitrophenylhydrazine, m. p. 144°).

Acetic anhydride (0·50 mole) and aluminium chloride (1·1 mole) provided identical products.

Propene and Crotonoyl Chloride.—Crotonoyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated as above; absorption of propene proceeded readily at 25°, ceasing sharply after 6 l. The product, isolated as above, was dipropenyl ketone (11 g.), b. p. 62—63°/16 mm. (Found: C, 85·3; H, 9·0. Calc. for $C_7H_{10}O$: C, 85·5; H, 9·1%). A sample (1·50 g.) in ethanol (10 ml.) absorbed hydrogen (596 ml. corr. to S.T.P. Calc. for $C_7H_{10}O$: 2 mol., 611 ml.) in the presence of palladium). The reduced product gave a semicarbazone, m. p. and mixed m. p. 132°.

3,4-Dimethylcyclopent-2-en-1-one.—Dipropenyl ketone (10 g.) was added to a solution of phosphoric acid (8 g.) in 98% formic acid (16 g.), and the mixture was kept at 90° for 4 hr. under nitrogen, then poured into water and extracted with ether. After the solvent had been removed, distillation gave 3,4-dimethylcyclopent-2-en-one (6 g.), b. p. 70°/12 mm. [2,4-*dinitrophenylhydrazone*, m. p. 210—212° (Found: C, 53·6; H, 4·9; N, 19·6. $C_{13}H_{14}N_4O_4$ requires C, 53·8; H, 4·8; N, 19·4%)]. The product (2·0 g.) in ethanol (10 ml.) absorbed hydrogen (410 ml. corr. to S.T.P. Calc. for $C_7H_{10}O$: 1 mol., 403 ml.) in the presence of palladium (0·1 g.). The reduced product, 3,4-dimethylcyclopentanone gave a 2,4-*dinitrophenylhydrazone*, m. p. 140° (Found: C, 53·1; H, 5·5; N, 19·6. $C_{13}H_{16}N_4O_4$ requires C, 53·4; H, 5·5; N, 19·4%), and a *semicarbazone*, m. p. 221° (Found: C, 56·2; H, 9·3; N, 24·6. $C_8H_{13}N_3O$ requires C, 56·5; H, 8·8; N, 24·8%).

Attempted cyclisation of divinyl ketone to yield cyclopentenone and of propenyl vinyl ketone to yield a methylcyclopentenone resulted in polymerisation.

Propene and β-Chloropropionyl Chloride.—β-Chloropropionyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated as in the previous experiment. Absorption was slow and, at 35°, 6 l. were absorbed in 1 hr. The mixture was decomposed and distillation of the product gave propenyl vinyl ketone (10·5 g.), b. p. 57—58°/16 mm. (Found: C, 74·8; H, 8·25. Calc. for C_6H_8O: C, 75·0; H, 8·3%). A sample (2·50 g.) in ethanol (20 ml.) absorbed hydrogen (1065 ml., corr. to S.T.P. Calc. for C_6H_8O: 2 mol., 1080 ml.) in the presence of palladium. The reduced product, ethyl propyl ketone, gave a 2,4-dinitrophenylhydrazone, m. p. 132°.

Propene and β-Methoxycarbonylpropionyl Chloride.—β-Methoxycarbonylpropionyl chloride

(0·25 mole) and aluminium chloride (0·30 mole) were treated as above. Absorption of propene was rapid at 25° and almost ceased after 6 l. The product, isolated as above, provided methyl 4-oxohept-5-enoate (14 g.), b. p. 105°/10 mm. A sample (2·00 g.) in ethanol (10 ml.) absorbed hydrogen (300 ml. corr. to S.T.P. Calc. for $C_8H_{12}O_3$: 1 mol., 290 ml.) in the presence of palladium. The reduced product gave a semicarbazone, m. p. and mixed m. p. 108° (Found: N, 19·2. Calc. for $C_9H_{17}N_3O_3$: N, 19·5%).

Ethylene and β-Chloropropionyl Chloride.—β-Chloropropionyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated with ethylene as described by Baddeley, Taylor, and Pickles.[1] The product, di-2-chloroethyl ketone (16 g.), was distilled rapidly from an excess of anhydrous sodium carbonate, giving divinyl ketone, b. p. 30°/16 mm. (7·5 g.). A sample (2·00 g.) in ethanol (10 ml.) absorbed hydrogen (1080 ml. corr. to S.T.P. Calc. for C_5H_6O: 2 mol., 1092 ml.). The product, dipropyl ketone, readily gave a 2,4-dinitrophenylhydrazone, m. p. 156°.

Ethylene and Crotonoyl Chloride.—Crotonoyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated as in the reaction with propene. Absorption of ethylene occurred readily at 25—30° and almost ceased after 12 l. Distillation of the residue provided propenyl vinyl ketone (12·5 g.), b. p. 57°/16 mm., identical with that obtained in the reaction with propene.

n-Propyl Iodide and Acetyl Chloride.—Acetyl chloride (0·25 mole) was added to a suspension of aluminium chloride (0·30 mole) in methylene chloride (100 ml.). The complex was decanted from excess of chloride, and n-propyl iodide (0·25 mole) was added at 40°, some evolution of hydrogen chloride and hydrogen iodide occurring, but not vigorously. After 3 hr. the mixture was decomposed, the organic layer dried (Na_2SO_4), and the solvent removed. The residue was propyl iodide. In the presence of excess of aluminium chloride (0·10 mole), iodine was liberated and a product (6·5 g.), b. p. −40°, was collected in a carbon dioxide–methanol trap. The product (propane) did not decolorise bromine water.

Isopropyl Bromide and Acetyl Chloride.—To the acetyl chloride–aluminium chloride complex (0·25 mole) as above, isopropyl bromide (0·25 mole) was added slowly at room temperature; little reaction occurred. At 40°, hydrogen bromide was copiously evolved and reaction was complete after 1 hr. The mixture was poured into dilute hydrochloric acid and ice, the organic layer separated and dried (Na_2SO_4), and the solvent removed. Distillation of the residue gave methyl propenyl ketone (9 g.), b. p. 48°/15 mm. (2,4-dinitrophenylhydrazone, m. p. 157°).

We thank Dr. G. Baddeley for his interest.

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259. *Synthetical Applications of Activated Metal Catalysts. Part XII.*[1] *The Preparation of Symmetrically Substituted 2,2′-Bipyridyls.*

By W. H. F. SASSE and C. P. WHITTLE.

The action of W7-J Raney nickel catalyst on ten substituted pyridines has been examined. 3- and 4-Alkyl groups facilitate the formation of 2,2′-bipyridyls, but electron-attracting groups in these positions or 2-methyl groups have the opposite effect. The structures of 2,2′-bipyridyls derived from 3-substituted pyridines are discussed.

THE formation of some disubstituted 2,2′-bipyridyls from monosubstituted pyridines under the influence of a degassed Raney nickel catalyst has been described earlier.[2] In view of the potential value of substituted 2,2′-bipyridyls as chelating agents, this work has been repeated and extended.

When refluxed over W7-J Raney nickel, β-picoline, γ-picoline, β-collidine, and 4-ethylpyridine gave biaryls in higher yields than did pyridine itself.[3] This finding agrees with

[1] Part XI, Badger, Jackson, and Sasse, *J.*, 1960, 4438.
[2] Badger and Sasse, *J.*, 1956, 616.
[3] Sasse, *J.*, 1959, 3046.

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the view that chemisorption of the simple pyridines on the catalyst precedes dimerisation,[2] as an increase in basicity will facilitate chemisorption.[4] The yields of the biaryls from the higher-boiling 4-phenylpyridine and β-collidine were higher in reactions under reduced pressure (reflux temperature, about 140°), an effect also observed in the quinoline series where secondary reactions of the biaryls occur at higher temperatures.[5] Although the yield of the diester obtained previously from ethyl nicotinate could be improved by working without a solvent and under reduced pressure, less than one-third of the quantity of biaryl obtainable from pyridine itself was isolated. 5-Benzoylpyridine (in boiling xylene) gave only traces of the bipyridyl, and no biaryl was obtained from ethyl isonicotinate, probably owing to the decreased basicity of these pyridine derivatives. The inhibiting effect of a 2-methyl group has been noted earlier,[2] but it has now been found that the small quantities of the biaryls derived from α-picoline and 2,4-lutidine are accompanied by traces of bipyridyls which do not contain 6,6′-methyl groups as they give stable iron(II) chelate compounds [6] (see Experimental part). Similarly, γ-collidine reacted under forcing conditions, to give a complex mixture from which 2,4-lutidine was separated by gas–liquid chromatography. The elimination of methyl groups from positions adjacent to the nitrogen atom occurs also in the quinoline series.[5]

All the biaryls obtained during the present work form chelate compounds with either ferrous or cuprous ions, and are therefore considered to be derivatives of 2,2′-bipyridyl. Structural ambiguities can arise only with 3-substituted pyridines which may be expected to give as many as three disubstituted 2,2′-bipyridyls. However, in each of the four cases examined, only one isomer could be detected. Of the three dimethyl-2,2′-bipyridyls which can be derived from β-picoline, the 3,5′-isomer appears to be unknown. 3,3′-Dimethyl-2,2′-bipyridyl was reported by Case to be a liquid [7] which forms a labile iron(II) chelate compound ($\lambda_{max.}$ at 526 mμ).[8] Case also prepared the 5,5′-isomer by two different routes but he did not disclose its properties; [7] however, Cagle and Smith [8] determined the absorption maximum of its iron(II) complex (at 510 mμ), and Case converted this base into dimethyl 2,2′-bipyridyl-5,5′-dicarboxylate. Our dimethyl-2,2′-bipyridyl also had these properties and is therefore regarded as the 5,5′-dimethyl isomer. Moreover, the acid obtained from it by oxidation is now found to be identical with that isolated from the reaction with nicotinic acid or its ethyl ester, thus confirming the structure suggested earlier.[2] Comparison of the ultraviolet spectra of these bipyridyls with the spectra of corresponding biphenyls supports this assignment (see Experimental part). Substitution in the 5,5′-positions is similarly indicated for the 2,2′-bipyridyls obtained from 3-benzoylpyridine and β-collidine. This substitution pattern is expected to be preferred for steric reasons, provided that there is some freedom for rotation around the nickel–nitrogen bonds in the adsorbed species.[5] The biaryls obtained from γ-picoline and β-collidine were further characterised by the preparation of bis-styryl derivatives.

Except for ethyl isonicotinate all 3- and 4-substituted pyridines gave rise to small quantities of materials containing nickel: [2,9] these substances are being examined.

Experimental

Starting Materials.—These were prepared by standard procedures except for the picolines, collidines, and the 2,4-lutidines. These bases were freed from pyrrolic constituents and fractionally distilled before use.[3]

Paper Chromatography.—The method described for bases in Part VIII [10] was used.

[4] Devereux, Payne, and Peeling, *J.*, 1957, 2845.
[5] Sasse, *J.*, 1960, 526.
[6] Brandt, Dwyer, and Gyarfas, *Chem. Rev.*, 1954, **54**, 959.
[7] Case, *J. Amer. Chem. Soc.*, 1946, **68**, 2574.
[8] Cagle and Smith, *J. Amer. Chem. Soc.*, 1947, **69**, 1860.
[9] Sargeson and Sasse, *Proc. Chem. Soc.*, 1958, 150.
[10] Sasse, *J.*, 1960, 526.

Ultraviolet Spectra.—Unless otherwise stated, these were determined for EtOH solutions on an Optica CF-4 recording spectrophotometer.

General Procedure.—Unless otherwise stated, each reaction was carried out by refluxing the base (150 c.c.) over W7-J Raney nickel catalyst [3] (prepared from 125 g. of alloy) for 50 hr. The bipyridyls were isolated as described for 2,2′-bipyridyl,[3] but hot benzene was used for the extraction of the catalyst. In some experiments different procedures were used. These are described below:

α-Picoline. 6,6′-Dimethyl-2,2′-bipyridyl, which separated from light petroleum as colourless needles (0·9 g.), m. p. 88·5—89·5° (lit.,[2,11] m. p. 89—90°), $\lambda_{max.}$ (log ε) at 238 (3·99) and 292 mμ (4·23), reacted with cuprous ions to give an orange chelate compound, but no colour was produced with ferrous ions. However, the liquors of its crystallisation formed a red chelate compound with ferrous ions.

β-Picoline. 5,5′-Dimethyl-2,2′-bipyridyl (Found: C, 78·5; H, 6·5; N, 15·0. Calc. for $C_{12}H_{12}N_2$: C, 78·2; H, 6·6; N, 15·2%) crystallised in colourless needles (53 g.) (from ethanol), m. p. 114·5—115°, R_F 0·66, $\lambda_{max.}$ (log ε) at 245 (4·05) and 290 mμ (4·18). 2,2′-Dimethylbiphenyl absorbs at 227 mμ (3·78) (point of inflexion),[12] 2,4′-dimethylbiphenyl at 240 mμ (4·07),[13] and 4,4′-dimethylbiphenyl at 254·5 mμ (4·32).[11] The bipyridyl forms a stable red iron(II) chelate compound ($\lambda_{max.}$ at 510 mμ; lit.,[8] 510 mμ). It did not form a styryl derivative when heated with benzaldehyde. Oxidation with potassium permanganate and esterification with methanol and sulphuric acid yielded dimethyl 2,2′-bipyridyl-5,5′-dicarboxylate (Found: C, 61·5; H, 4·4; N, 10·3. Calc. for $C_{14}H_{12}N_2O_4$: C, 61·8; H, 4·4; N, 10·3%), m. p. 261—262° (lit.,[7] m. p. 261—262°) alone or mixed with a sample derived from the dicarboxylic acid formed by degassed Raney nickel from nicotinic acid.[3]

γ-Picoline. 4,4′-Dimethyl-2,2′-bipyridyl (Found: C, 78·4; H, 6·6; N, 15·3. Calc. for $C_{12}H_{12}N_2$: C, 78·2 H, 6·6; N, 15·2%) separated from ethanol in colourless needles (56 g.), m. p. 170—172° (lit.,[7] m. p. 171—172°), $\lambda_{max.}$ (log ε) at 241 (3·97) and 282·5 mμ (4·12), R_F 0·44. Condensation with benzaldehyde by the method of Staněk and Horák [14] gave *4,4′-distyryl-2,2′-bipyridyl* (Found: C, 86·5; H, 5·6; N, 8·0. $C_{26}H_{20}O_2$ requires C, 86·6; H, 5·6; N, 7·8%) in 93% yield. This base formed a colourless powder, m. p. 268·5—269·5° (from ethyl benzoate–pyridine). Hydrogenation over 5% palladium–charcoal (500 lb.; 65°) in acetic acid gave *4,4′-diphenethyl-2,2′-bipyridyl* (Found: C, 85·5; H, 6·4; N, 7·7. $C_{26}H_{24}N_2$ requires C, 85·7; H, 6·6; N, 7·7%), crystallising in needles, m. p. 147·5—148°, from ethanol. All three bipyridyls derived from γ-picoline reacted with ferrous ions, to give red chelate compounds.

4-Ethylpyridine. 4,4′-Diethyl-2,2′-bipyridyl formed a colourless oil (48 g.), b. p. 130°/0·2 mm. (lit.,[2] b. p. 210°/30 mm.). Its *monopicrate* crystallised from ethanol as yellow plates, m. p. 153—154° (decomp.), alone or mixed with a sample obtained from the bipyridyl analysed earlier [3] (Found for picrate: C, 54·65; H, 4·4; O, 25·5. $C_{20}H_{19}N_5O_7$ requires C, 54·4; H, 4·3; O, 25·4%).

β-Collidine. (*a*) *5,5′-Diethyl-4,4′-dimethyl-2,2′-bipyridyl* (Found: C, 80·3; H, 8·4; N, 11·5. $C_{16}H_{20}N_2$ requires C, 80·0; H, 8·4; N, 11·7%) crystallised in colourless needles (25 g.) (from ethanol), m. p. 141·5—142°, $\lambda_{max.}$ (log ε) at 247 (4·15) and 290 mμ (4·32), R_F 0·93.

(*b*) Reaction under reduced pressure at 140° gave an improved yield of the bipyridyl (53 g.). This base with benzaldehyde gave, in 92% yield, *5,5′-diethyl-4,4′-distyryl-2,2′-bipyridyl* (Found: C, 86·1; H, 6·8; N, 6·7. $C_{30}H_{28}N_2$ requires C, 86·5; H, 6·8; N, 6·7%), colourless plates (from ethanol), m. p. 182—183°. This derivative was hydrogenated as described above, giving in 98% yield *5,5′-diethyl-4,4′-diphenethyl-2,2′-bipyridyl* (Found: C, 85·9; H, 7·5; N, 6·75. $C_{30}H_{32}N_2$ requires C, 85·7; H, 7·7; N, 6·7%). After crystallisation from ethanol it formed colourless dimorphic needles, m. p. 133—135° amd 142—143°. All three bipyridyls derived from β-collidine formed red iron(II) chelate compounds.

2,4-Lutidine. After removal of all materials boiling up to 100°/20 mm. the residue was chromatographed on alumina. All materials eluted by light petroleum were distilled. The fraction of b. p. 110—130°/1 mm. formed a colourless oil (10 g.) from which separated 4,4′,6,6′-tetramethyl-2,2′-bipyridyl (0·83 g.) (Found: C, 79·4; H, 7·7; N, 13·2. Calc. for $C_{14}H_{16}N_2$:

[11] Willinck and Wibaut, *Rec. Trav. chim.*, 1935, **54**, 275.
[12] Johnson, *J.*, 1957, 4155.
[13] Catalogue of Ultraviolet Spectral Data of the American Petroleum Inst., Research Project 44, no. 708.
[14] Staněk and Horák, *Coll. Czech. Chem. Comm.*, 1951, **15**, 1037 (*Chem. Abs.*, 1952, **46**, 7100).

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C, 79·2; H, 7·6; N, 13·2%), needles (from light petroleum), m. p. 142·5—143° (lit.,[15] m. p. 144—145°), $\lambda_{max.}$ (log ε) at 247 (4·15) and 290 mμ (4·3), R_F 0·25. This base formed an orange chelate compound with cuprous ions, $\lambda_{max.}$ 450 mμ (lit.,[15] $\lambda_{max.}$ 450 mμ), but it failed to produce a colour with ferrous ions. However, the liquors of its crystallisation gave a red colour with ferrous ions, and paper chromatography revealed the presence of a base with the R_F of 4,4′-dimethyl-2,2′-bipyridyl.

2,4,6-*Collidine*. The reaction was continued for 200 hr. After removal of the catalyst all material boiling up to 175° was distilled off (141 c.c.). Examination of the residue by paper chromatography showed the presence of at least six bases, five of which gave red stains on being sprayed with ferrous sulphate solution. The distillate was redistilled to give the fractions: (*a*) b. p. 98—100° (4 c.c.); (*b*) b. p. 140—164° (3 c.c.); (*c*) b. p. 164—167° (5 c.c.); (*d*) b. p. 167—168° (11 c.c.); and a residue (118 c.c.). Fraction (*a*) contained largely water. Gas–liquid chromatography [5] of fractions (*b*), (*c*), and (*d*) at 90° (flow-rate 1·2 l. per hr. of nitrogen) showed that, besides collidine (retention time 14·1 min.), 2,4-lutidine (retention time 9·3 min.) was present. From the areas under the peaks it was estimated that 3—4% of lutidine was formed in this reaction. Both bases were separated by gas chromatography and identified by their infrared spectra. A third component (retention time 6·3 min.) occurred in fractions (*b*) and (*c*) in quantities which did not allow its isolation.

4-*Phenylpyridine*. (*a*) 4-Phenylpyridine [16] (63 g.) gave 4,4′-diphenyl-2,2′-bipyridyl (Found: C, 85·5; H, 5·2; N, 9·0. Calc. for $C_{22}H_{16}N_2$: C, 85·7; H, 5·2; N, 9·1%) which separated from light petroleum–benzene as colourless needles (3·1 g.), m. p. 187—188° (lit.,[17] m. p. 187—188°), $\lambda_{max.}$ (log ε) 251 mμ (4·63), and formed a red iron(II) chelate compound.

(*b*) Under reduced pressure at 130—150°, 4-phenylpyridine (100 g.) gave 4,4′-diphenyl-2,2′-bipyridyl (5 g.).

Ethyl nicotinate. Under reduced pressure at 145° diethyl 2,2′-bipyridyl-5,5′-dicarboxylate (11 g.), m. p. 149° (lit.,[2] m. p. 148—149°), was obtained. It had $\lambda_{max.}$ (log ε) at 250 (4·12), 256 (4·14), and 300 mμ (4·45). The diacid absorbs at 290 mμ (4·48).[18]

3-*Benzoylpyridine*. The ketone (32 g.) was refluxed in xylene (50 c.c.) for 45 hr., to give colourless plates (0·14 g.) of 5,5′-*dibenzoyl*-2,2′-*bipyridyl* (Found: C, 79·2; H, 4·4; N, 7·9. $C_{24}H_{16}N_2O_2$ requires C, 79·1; H, 4·4; N, 7·7%), m. p. 209·5—211° (from benzene–ethanol), $\nu_{max.}$ 1660 cm.$^{-1}$ (in Nujol), $\lambda_{max.}$ (log ε) 260 (4·21), 264 (4·23), and 311 mμ (4·48). 4,4′-Dibenzoylbiphenyl [18] has $\lambda_{max.}$ (log ε) at 250 (4·20), 256 (4·24), 262 (4·24), and 299 mμ (4·76) (in dioxan). The bipyridyl gave a blue-violet iron(II) chelate compound when dissolved in glacial acetic acid.

Ethyl isonicotinate. No derivative of 2,2′-bipyridyl could be detected after this ester had been refluxed for 76 hr. over the catalyst.

Formation of Nickel Complexes.[3]—Small quantities (1—3 g.) of nickel complexes were obtained from the reactions involving β-picoline, γ-picoline, β-collidine, 4-ethylpyridine, 4-phenylpyridine, and ethyl nicotinate. Except for the reaction with ethyl isonicotinate, *p*-dimethylaminobenzaldehyde indicated the presence of small quantities of pyrroles in every experiment.

We thank the Petroleum Research Fund, administered by the American Chemical Society, for a grant, also Professor G. M. Badger and Dr. H. J. Rodda for their interest, Mr. A. G. Moritz for infrared spectra, and the C.S.I.R.O. for a Maintenance Grant (to C. P. W.).

University of Adelaide, South Australia. [*Received, October 12th*, 1960.]

[15] Linell, *J. Org. Chem.*, 1957, **22**, 1691.
[16] Schmidle and Mansfield, *J. Amer. Chem. Soc.*, 1956, **78**, 1702.
[17] Case and Kasper, *J. Amer. Chem. Soc.*, 1956, **78**, 5842.
[18] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.
[19] Schlenk and Brauns, *Ber.*, 1915, **48**, 716.

260. *Perfluoroalkyl Derivatives of Nitrogen. Part IX.* The Reaction of Trifluoronitrosomethane with Some Unsymmetrical Olefins.†*

By D. A. Barr, R. N. Haszeldine, and C. J. Willis.

Trifluoronitrosomethane reacts with an olefin $CF_2{:}CXY$ ($CF_2{:}CFCl$, $CF_2{:}CCl_2$, $CF_2{:}CF{\cdot}CF_3$) to give an oxazetidine $CF_3{\cdot}\overset{\frown}{N{\cdot}O{\cdot}CXY{\cdot}CF_2}$ and a viscous or elastomeric 1 : 1 copolymer $[{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{\cdot}]_n$. The direction of addition to the olefin in formation of oxazetidine is opposite to that involved in copolymer formation. Pyrolysis of oxazetidine and of polymer yields compounds such as $CF_3{\cdot}N{:}CF_2$, $CF_3{\cdot}N{:}CF{\cdot}CF_3$, $CF_3{\cdot}N{:}CFCl$, and $CF_3{\cdot}N{:}CCl_2$; initial cleavage of the N–O bond in oxazetidine or polymer is followed by degradation of the polyhalogeno-alkoxy-radical by acyl halide formation. The elastomer from tetrafluoroethylene and trifluoronitrosomethane, the first reported with the –N–O–C–C– backbone, retains its flexibility at −30°. Reaction schemes are advanced for the formation of 1 : 1 copolymer by a low-temperature free-radical process, and for oxazetidine formation involving an initial 1 : 1 molecular complex of the Diels–Alder type. Trifluoronitrosomethane is considered as a free-radical source through its rapid reaction with nitric oxide, even at temperatures below −100°, to give ultimately the compounds $CF_3{\cdot}NO_2$, $(CF_3)_2N{\cdot}O{\cdot}NO$, and CO_2.

Trifluoronitrosomethane reacts readily with tetrafluoroethylene to give two products,[1] an oxazetidine (I) and a 1 : 1 copolymer (II); the polymer predominates in reactions

(I) (II)

at room temperature, and the oxazetidine at higher temperatures (*ca.* 100°). When pyrolysed, each of these compounds gives, quantitatively, an equimolar mixture of perfluoro(methylenemethylamine), $CF_3{\cdot}N{:}CF_2$, and carbonyl fluoride. Both radical and ionic intermediates could explain the effects of varying reaction conditions, with the former slightly favoured.[1]

The reaction of trifluoronitrosomethane with some unsymmetrical fluoro-olefins has now been studied in order to throw further light on the mechanism of formation of the unusual compounds (I) and (II). The olefins $CF_2{:}CXY$, where (i) X = F, Y = Cl, (ii) X = Y = Cl, and (iii) X = F, Y = CF_3, all yield an oxazetidine and a 1 : 1 copolymer.[2] In each case two structures are clearly possible for the oxazetidine and for the polymer,

Olefin	Oxazetidine	Copolymer
$CF_2{:}CFCl$	$CF_3{\cdot}\overset{\frown}{N{\cdot}O{\cdot}CFCl{\cdot}CF_2}$	$[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CFCl-]_n$
$CF_2{:}CCl_2$	$CF_3{\cdot}\overset{\frown}{N{\cdot}O{\cdot}CCl_2{\cdot}CF_2}$	$[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CCl_2-]_n$ predominantly, plus $[-N(CF_3){\cdot}O{\cdot}CCl_2{\cdot}CF_2-]_n$
$CF_2{\cdot}CF{:}CF_2$	$CF_3{\cdot}\overset{\frown}{N{\cdot}O{\cdot}CF(CF_3){\cdot}CF_2}$ 90%	$[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF(CF_3)-]_n$ 90%
	$CF_3{\cdot}\overset{\frown}{N{\cdot}O{\cdot}CF_2{\cdot}CF(CF_3)}$ 10%	$[-N(CF_3){\cdot}O{\cdot}CF(CF_3){\cdot}CF_2-]_n$ 10%

depending on the direction of addition of trifluoronitrosomethane to the olefin. This direction of addition has been established by pyrolysis and identification of the products.

* Part VIII, Griffin and Haszeldine, *J.*, 1960, 1398.

† Presented at the American Chemical Society, Atlantic City, 1956, Abs. 13M; Symposium on Fluorine Chemistry, Birmingham, 1959; see also *Proc. Chem. Soc.*, 1959, 230.

[1] Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

[2] Barr, Haszeldine, and Willis, *Proc. Chem. Soc.*, 1959, 230.

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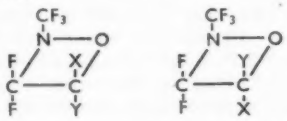
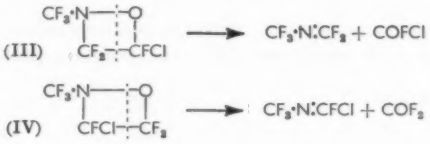
The results are summarised in the annexed Table, from which two notable features emerge: (i) the direction of addition is specific both for the formation of oxazetidine ($CF_3{\cdot}N{\cdot}O{\cdot}CFX{\cdot}CF_2$) and for formation of the copolymer ($[-N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY-]_n$), and (ii) the direction of addition involved in formation of the oxazetidine is opposite to that involved in formation of the copolymer.

Whether the oxazetidine $CF_3{\cdot}N{\cdot}O{\cdot}CXY{\cdot}CF_2$ is capable of existence in two forms (as shown) has yet to be determined.

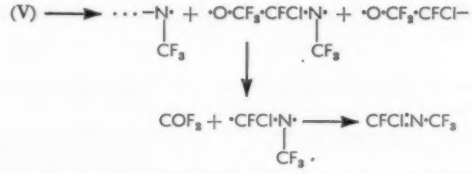


Chlorotrifluoroethylene reacted with trifluoronitrosomethane under the mild conditions previously used for tetrafluoroethylene, *i.e.*, in sealed glass or silica tubes under 5—10 atm. pressure and in absence of light or air; formation of the oxazetidine was favoured at 70°, and at 20° the 1 : 1 copolymer predominated. Pyrolysis of the oxazetidine at 550° gave only equimolar amounts of the compounds $CF_3{\cdot}N{:}CF_2$ and COFCl, thus suggesting structure (III) rather than (IV):

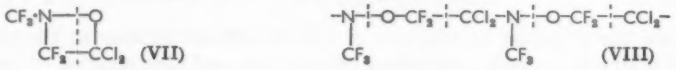


By contrast, pyrolysis of the polymer gave equimolar amounts of the compounds $CF_3{\cdot}N{:}CFCl$ and COF_2, with only traces of the compound $CF_3{\cdot}N{:}CF_2$; structure (V) thus predominates considerably over (VI).

Breakdown of oxazetidine and polymer is believed to be initiated by N–O cleavage, followed by elimination of carbonyl halide from the polyhalogeno-alkoxy-radical [1,3] so produced, *e.g.*:



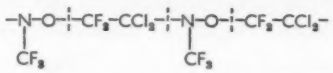
1,1-Dichlorodifluoroethylene reacted with trifluoronitrosomethane under similar conditions. The oxazetidine yielded the compounds $CF_3{\cdot}N{:}CF_2$ and $COCl_2$ on pyrolysis, whereas



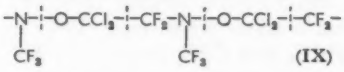
the polymer gave mainly the compounds $CF_3{\cdot}N{:}CCl_2$ and COF_2. Structures (VII) and (VIII) thus predominate. The carbonyl chloride produced by pyrolysis of the oxazetidine dissociated to some extent into carbon monoxide and chlorine. Cleavage of compound

[3] Francis and Haszeldine, *J.*, 1955, 2151; Haszeldine and Nyman, *J.*, 1959, 387, 420, 1084.

(VII) in the other direction also occurred to a very small extent, to give the original reactants $CF_3{\cdot}NO$ and $CF_2{:}CCl_2$. The last two compounds were also formed, to an extent of 5—10%, by pyrolysis of the polymer, revealing an alternative breakdown route:



Although the copolymer has mainly structure (VIII), some of the copolymer (IX) is present, since its pyrolysis products $CF_3{\cdot}N{:}CF_2$ and $COCl_2$ were detected. An alternative,[3] though less likely, explanation is that the polymer is in fact entirely of structure (VIII),



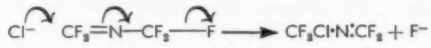
(IX)

and the pyrolysis by-products $CF_3{\cdot}N{:}CF_2$ and $COCl_2$ result from formation of the original reactants $CF_3{\cdot}NO$ and $CF_2{:}CCl_2$ which, under the pyrolysis conditions, react to give the oxazetidine (VII), breakdown of which would give $CF_3{\cdot}N{:}CF_2$ and $COCl_2$.

The compound $CF_3{\cdot}N{:}CCl_2$ was identical with that obtained by reaction of the compound $CF_3{\cdot}N{:}CF_2$ with an equimolar amount of anhydrous hydrogen chloride. The overall reaction may be represented:

$$3CF_3{\cdot}N{:}CF_2 + 2HCl \longrightarrow CF_3{\cdot}N{:}CCl_2 + 2(CF_3)_2NH$$

Much unchanged hydrogen chloride was recovered, but only traces of the compound $CF_3{\cdot}N{:}CF_2$ remained, and the compound $CF_3{\cdot}N{:}CFCl$ was only a minor ultimate product. The amine $CF_3{\cdot}NH{\cdot}CF_2Cl$ is probably the initial product, formed by a relatively slow addition, followed by rapid loss of hydrogen fluoride to give $CF_3{\cdot}N{:}CFCl$. It was known [4] that hydrogen fluoride forms the amine $(CF_3)_2NH$ from the compound $CF_3{\cdot}N{:}CF_2$ at higher temperatures, and the present result revealed that the high temperature previously employed was unnecessary; this was confirmed experimentally, since anhydrous hydrogen fluoride and perfluoro(methylenemethylamine) react rapidly and quantitatively at room temperature to give bistrifluoromethylamine. The compound $CF_3{\cdot}N{:}CFCl$ also reacts with anhydrous hydrogen chloride, but the amine $CF_3{\cdot}NH{\cdot}CFCl_2$ again loses hydrogen fluoride, to give the compound $CF_3{\cdot}N{:}CCl_2$. The reaction of the last compound with hydrogen chloride at room temperature is very slow. Loss of hydrogen fluoride from the amine $CF_3{\cdot}NH{\cdot}CF_2Cl$ or $CF_3{\cdot}NH{\cdot}CFCl_2$ does not involve the fluorine of the CF_3 group, since the compounds $CF_2Cl{\cdot}N{:}CF_2$ and $CFCl_2{\cdot}N{:}CF_2$ were not ultimate products, although the possibility that they were formed initially:



and underwent rapid rearrangement of the allylic type:

$$CF_2Cl{\cdot}N{:}CF_2 \rightleftharpoons CFCl{:}N{\cdot}CF_3$$

cannot be excluded completely.

As expected, the $N{:}CF_2$ stretching vibration is markedly affected by replacement of fluorine by chlorine: $CF_3{\cdot}N{:}CF_2$ 5·53, $CF_3{\cdot}N{:}CFCl$ 5·74, $CF_3{\cdot}N{:}CCl_2$ 5·99 μ.

Examination was made of the possibility of the reactions,

$$CF_3{\cdot}N{:}CF_2 + COCl_2 \rightleftharpoons CF_3{\cdot}N{:}CFCl + COFCl \rightleftharpoons CF_3{\cdot}N{:}CCl_2 + COF_2$$

occurring at the high temperatures used in the pyrolyses, since such exchange reactions would vitiate structural assignments based on the pyrolysis products actually isolated; under the conditions used, the pairs of compounds $CF_3{\cdot}N{:}CF_2 + COCl_2$, $CF_3{\cdot}N{:}CFCl +$

[4] Barr and Haszeldine, *J.*, 1955, 2532.

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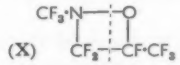
COF_2, or $CF_3{\cdot}N{:}CCl_2 + COF_2$ failed to react to give even traces of products resulting from an exchange reaction.

Hexafluoropropene failed to react with trifluoronitrosomethane under the conditions used for the other olefins; but at higher pressures and 100° reaction occurred, to give both oxazetidine and a 1 : 1 copolymer; the use of temperatures much above 100° is precluded



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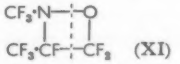
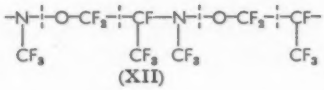


(XI)

by the self-decomposition of trifluoronitrosomethane. Pyrolysis of the oxazetidine gave the compounds $CF_3{\cdot}N{:}CF_2$ and $CF_3{\cdot}COF$ arising from (X) in 90% yield. The other possible oxazetidine (XI) was a minor constituent (10%) as measured by the amounts of the compounds $CF_3{\cdot}N{:}CF{\cdot}CF_3$ and COF_2 produced. The extent of these alternative modes of addition was reversed in the 1 : 1 copolymer, which yielded compounds $CF_3{\cdot}N{:}CF{\cdot}CF_3$ and COF_2 (90%) from (XII), and compounds $CF_3{\cdot}N{:}CF_2$ and $CF_3{\cdot}COF$ (10%) from (XIII).



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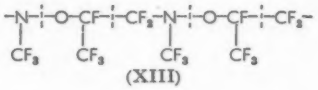

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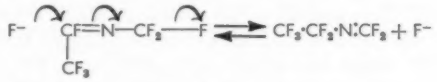
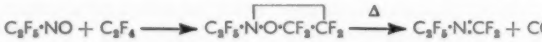
Perfluoro(ethylidenemethylamine) is the first compound of type $R_FN{:}CFR_F$ to be prepared unambiguously. The possibility that isomerisation by rearrangement of the allylic type might have occurred during pyrolysis:



was eliminated by synthesis of its isomer as follows:



It can be safely assumed that no rearrangement will occur during the pyrolysis to give perfluoro(methylene-ethylamine), since the analogous reaction

has been investigated [1] and the identity of the product confirmed by its hydrolysis to pentafluoropropionic acid. The isomers differ appreciably in infrared spectrum (*e.g.*, cf. C:N stretching vibrations: $CF_3{\cdot}N{:}CF_2$ 5·53; $C_2F_5{\cdot}N{:}CF_2$ 5·52; $C_3F_7{\cdot}N{:}CF_2$ 5·51; $CF_3{\cdot}N{:}CF{\cdot}CF_3$ 5·60 μ) and in boiling point ($C_2F_5{\cdot}N{:}CF_2$ −6°; $CF_3{\cdot}N{:}CF{\cdot}CF_3$ −15°).

It was suggested earlier [1] that the compound of b. p. 12·3° reported as perfluoro(methylene-n-propylamine) $C_3F_7{\cdot}N{:}CF_2$ from pyrolysis of perfluorotripropylamine was in fact perfluoro(ethylidene-ethylamine) $C_2F_5{\cdot}N{:}CF{\cdot}CF_3$, or a mixture containing it, since the compound $C_3F_7{\cdot}N{:}CF_2$ of proved structure boiled at 25·6°. The new evidence supports this suggestion, and it is clear that a compound of type $R_FN{:}CF_2$ has a boiling point higher than that of its isomer $R'_FN{:}CFR''_F$.

Elastomer Formation from Trifluoronitrosomethane and Tetrafluoroethylene.—The first copolymer obtained from trifluoronitrosomethane and tetrafluoroethylene [1] was a viscous liquid, of molecular weight ⩾7000 as far as could be determined ebullioscopically with perfluoromethylcyclohexane as solvent. Later samples were weak elastomers with gel-like appearance,[1] and the factors that affect formation of oil or of elastomer were therefore examined, particularly since dichlorodifluoroethylene also gave weak elastomers, whereas trifluoroethylene gave a strong elastomer [2] very readily. The main factors involved in

formation of the elastomer $[-N(CF_3)\cdot O\cdot CF_2\cdot CF_2-]_n$ are purity of reactants, reactant ratio, and reaction temperature and pressure; proper control of these leads to polymer of greater chain length and to the transition from viscous oil to elastomer.

Purity of the reactants is vital. Trifluoronitrosomethane needs to be free from trifluoroiodomethane, trifluoronitromethane, dinitrogen tetroxide, and nitric oxide. Each of these can stop the growth of a polymer radical—by abstraction by the radical of iodine from trifluoroiodomethane, by addition of the radical to the $CF_2\cdot NO_2$ group, or by direct combination of the radical with the radical NO_2 or NO. Air or moisture, which decompose the nitroso-compound, must be excluded. The fluoro-olefin must be pure and free from peroxides. Use of a molar reactant ratio close to 1 : 1 gives the best results, and in this the copolymerisation resembles polycondensations. Finally, a temperature in the region −20° to +20°, and conveniently 0°, leads to rapid combination of trifluoronitrosomethane and tetrafluoroethylene to give an elastomer. Use of a low temperature favours formation of polymer rather than oxazetidine, but is important in at least two other aspects: (*a*) provided that the pressure is high enough the reaction takes place mainly in the liquid phase; and (*b*) self-decomposition of trifluoronitrosomethane is minimised. As shown below, the self-decomposition of trifluoronitrosomethane yields, amongst other products, dinitrogen tetroxide and trifluoronitromethane, and these markedly affect the chain length of the polymer.

It is also possible to convert a viscous 1 : 1 copolymer of trifluoronitrosomethane and tetrafluoroethylene into an elastomer by heating the oil *in vacuo* at 50—150°; apparently polymer chains break and re-form under this ageing treatment, with possibly a small amount of cross-linking. The polymer system shows similarities to silicone or polyester polymers in this respect.

The elastomer from tetrafluoroethylene is a white translucent material reminiscent of a silicone rubber. It is the first to be reported with the −N−O−C−C− backbone, has good thermal stability at 200° in presence of air, and is apparently unaffected over long periods at 180°. Pyrolysis at 550° yields equimolar amounts of the compounds $CF_3\cdot N{:}CF_2$ and COF_2 as reported earlier.[1] The new elastomer is of particular interest in two respects which should make it of value in a number of applications. It remains flexible at −30°, indicating that rotation of the chain about the N−O bond, and the size of the trifluoromethyl side-chain, effectively prevent crystallisation; by contrast polytetrafluoroethylene is highly crystalline. The elastomer is also insoluble in the common solvents, as is the shorter-chain oily polymer,[1] but dissolves in perfluoromethylcyclohexane, although less readily than the oily polymer. Solvent and chemical resistance are thus extremely good.

$[\eta]$	1·0—2·0	Tensile strength	500 p.s.i.
Gehman T_{10}	−45°	Elongation at break	500—1000% at 25°
T_g	−54°		

Other properties of the polymer are summarised in the annexed Table. Precise calculation of the molecular weight of the polymer from the equation $[\eta] = KM^{\alpha}$ cannot be carried out, since the value of K, the constant depending on the solvent, is not known for the fluorocarbon solvent used (C_7F_{14}), and α has not been determined for other fluoropolymers. However, α usually lies between 0·6 and 0·8 for linear flexible molecules, and is 0·65 for polydimethylsiloxane (a polymer not unlike the trifluoronitrosomethane–tetrafluoroethylene copolymer) in toluene solution ($K = 2{\cdot}0 \times 10^{-4}$). An approximate molecular weight for the elastomeric copolymer of 500,000—1,500,000 is obtained by assuming $K \approx 2{\cdot}0 \times 10^{-4}$ and $\alpha = 0{\cdot}65$.

Reaction of Trifluoronitrosomethane with Nitric Oxide.—Pure trifluoronitrosomethane reacts very rapidly with liquid nitric oxide at temperatures well below −100°, and yields nitrogen, trifluoronitromethane, *O*-nitrosobistrifluoromethylhydroxylamine, $(CF_3)_2N\cdot O\cdot NO$, silicon tetrafluoride, and carbon dioxide. These can arise by the annexed scheme. Addition of two molecules of nitric oxide to the nitroso-group is followed by formation of the

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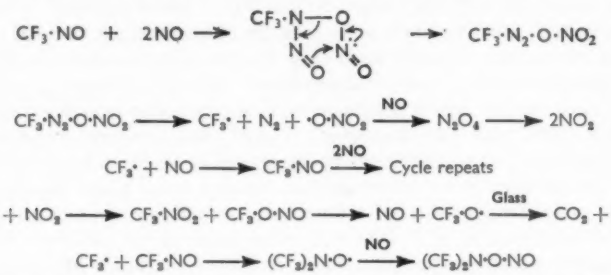
diazonium nitrate, which decomposes to nitrogen and dinitrogen tetroxide with formation of a CF_3 radical. A similar scheme has been used to interpret the reaction of nitric oxide with tetrafluoroethylene to give the compound $NO_2{\cdot}CF_2{\cdot}CF_2{\cdot}NO$.[6]

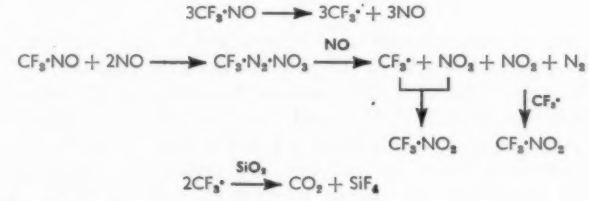
The same products are formed, though much more slowly, when trifluoronitrosomethane reacts with nitric oxide in the vapour phase; the slowness of the reaction is revealed by the fact that the nitroso-compound is prepared in 80% yield by the photochemical vapour-phase reaction of trifluoroiodomethane with an excess of nitric oxide.



The formation of nitric oxide from trifluoronitrosomethane itself ($CF_3{\cdot}NO \rightleftharpoons CF_3{\cdot} + NO$) occurs to some extent at room temperature, since pure trifluoronitrosomethane very slowly decomposes in the dark, even at −20°, to give the same products as were noted from the liquid-phase reaction with nitric oxide. The self-decomposition of trifluoronitrosomethane thus follows the reaction path indicated in the equations above. Cleavage of the C–N bond in the nitroso-compound is accelerated by heat or light. Decomposition of trifluoronitrosomethane at temperatures above 100° is relatively rapid, and its photochemical dimerisation to give the compound $(CF_3)_2N{\cdot}O{\cdot}NO$ at room temperature is easily achieved.

Thus, trifluoronitrosomethane can act as a source of free radicals by direct dissociation, or by reaction with nitric oxide; radicals such as $CF_3{\cdot}$, $CF_3{\cdot}O{\cdot}$, $(CF_3)_2N{\cdot}O{\cdot}$, or NO_2, produced at temperatures well below those normally associated with free-radical formation, are thus available for initiation of the copolymerisation of trifluoronitrosomethane with fluoro-olefins.

Thermal Decomposition of Trifluoronitrosomethane.—The blue colour of trifluoronitrosomethane completely disappears when the compound is heated at 100° for 14 days in glass, and a 48% yield of trifluoronitromethane results; carbon dioxide, silicon tetrafluoride, and nitrogen are the only other products. The reaction scheme suggested is based on that for the trifluoronitrosomethane–nitric oxide reaction:



The overall reaction is thus

$$4CF_3{\cdot}NO \longrightarrow 2CF_3{\cdot}NO_2 + N_2 + 2CF_3{\cdot}\ (\text{as } CO_2 + SiF_4)$$

where a disproportionation-type reaction oxidises half of the trifluoronitrosomethane to trifluoronitromethane at the expense of the other half, which is converted into nitrogen

[5] Pearlson and Hals, U.S.P. 2,643,267; *Chem. Abs.*, 1954, **48**, 6461.
[6] Birchall, Bloom, Haszeldine, and Willis, *Proc. Chem. Soc.*, 1959, 367.

and trifluoromethyl radicals, these radicals decomposing on the wall, as often observed before, to give carbon dioxide and silicon tetrafluoride. The 48% yield of trifluoronitromethane obtained is close to that expected (50%) by the above scheme.

Polymer Formation from Trifluoronitrosomethane and Olefins $CF_2{:}CXY$.—Earlier studies [1] showed that addition of quinol halved the rate of the $C_3F_7{\cdot}NO{-}C_2F_4$ reaction and decreased the polymer : oxazetidine ratio eight-fold. By contrast, addition of t-butyl peroxide, or exposure to ultraviolet light, increased the rate of reaction and doubled the polymer : oxazetidine ratio; surface effects seemed relatively unimportant. This evidence points to a free-radical mechanism for copolymer formation, although the facts that polymerisation occurred without deliberate addition of an initiator, and at temperatures near 0° could be taken to indicate a carbanion ionic mechanism.

All the evidence now available is in favour of a radical mechanism. *Initiation* probably occurs by formation of $CF_3{\cdot}$, $CF_3{\cdot}O{\cdot}$, $(CF_3)_2N{\cdot}O{\cdot}$, or NO_2 radicals by the self-decomposition of trifluoronitrosomethane, this decomposition being accelerated by heat, light, or presence of oxygen. These radicals, R·, then attack the trifluoronitrosomethane nitrogen atom:

$$R{\cdot} + CF_3{\cdot}N{:}O \longrightarrow R{\cdot}N(CF_3){\cdot}O{\cdot}$$

The direction of addition of a free radical to a nitroso-group is known from the free-radical dimerisation of trifluoronitrosomethane to give the compound $(CF_3)_2N{\cdot}O{\cdot}NO$.[7]

The 1 : 1 copolymers obtained from the unsymmetrical olefin $CF_2{:}CXY$ (X = F, Y = Cl; X = Y = Cl; X = F, Y = CF_3) are predominantly of one structure $[{-}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{-}]_n$ and this is consistent with the following propagation steps:

$$R{\cdot}N(CF_3){\cdot}\dot{O} + CF_2{:}CXY \longrightarrow R{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{\cdot}$$

$$R{\cdot}N(CF_3){\cdot}\dot{O} \xrightarrow{CF_2:CXY} R{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{\cdot} \xrightarrow{CF_3{\cdot}NO} R{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{\cdot}N(CF_3){\cdot}O{\cdot} \xrightarrow{CF_2:CXY} \text{etc.}$$

Free-radical addition to the olefins $CF_2{:}CXY$ is known to be on the carbon indicated: $*CF_2{:}CFCl$, $*CF_2{:}CCl_2$, $*CF_2{:}CF{\cdot}CF_3$.[8] The final polymer thus contains oxygen attached to the carbon atom of the olefin most susceptible to radical attack.

Oxazetidine Formation.—There is a similarity between oxazetidine ring formation and the Diels–Alder reaction. Both nitrogen and oxygen in the nitroso-compound contain unshared electrons, so that the N:O group is electron-rich and may be considered as equivalent to the diene of the Diels–Alder reaction; the fluoro-olefin has electron-withdrawing substituents and the double bond is electron-poor, thus being equivalent to the dienophile. Formation of a preliminary 1 : 1 molecular complex between the nitroso-compound and the fluoro-olefin would explain why the products contain equimolar amounts of the reactants as in the oxazetidine and the strictly 1 : 1 copolymer.

Formation of a 1 : 1 molecular complex in which (*a*) the nitrogen of trifluoronitrosomethane is vertically above the CF_2 carbon atom and at right angles to the plane of the F–C–F group of the olefin $CF_2{:}CXY$, and (*b*) the oxygen of trifluoronitrosomethane is vertically above the CXY carbon atom and at right angles to the plane of the X–C–Y group, could be assisted by overlap of an sp^2-orbital of nitrogen with that of fluorine in the CF_2 group. It should be noted that in all oxazetidines so far obtained from olefins of the $CF_2{:}CXY$ type, the nitrogen is attached to the CF_2 group.

When X and/or Y are bulky, *i.e.*, larger than fluorine, steric factors may also play a part, since models show that least steric interaction occurs between the CF_3 group of

[7] Haszeldine and Mattinson, *J.*, 1957, 1741.
[8] Haszeldine, *Ann. Reports*, 1954, **51**, 291.

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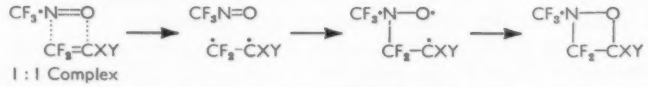
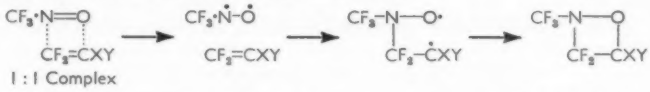
trifluoronitrosomethane and the atoms or groups X and Y when the nitrogen is vertically above the CF_2 group carbon atom, and the oxygen vertically above the CXY group carbon atom.

The step following complex formation may involve a molecular or four-centre process, but an argument based on radical intermediates will explain most of the observed facts. Thus, if complex formation involves, or is followed by, partial or complete diradical formation by the olefin to give $\dot{C}F_2{\cdot}\dot{C}XY$, then the more reactive of the species $-\dot{C}F_2$ or $-\dot{C}XY$ would attack the nitrogen of trifluoronitrosomethane to give the most stable diradical, ring closure in which affords the oxazetidine:

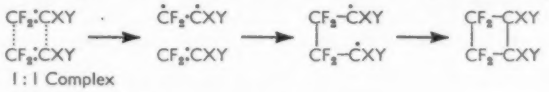


That a $-\dot{C}F_2$ radical is more reactive than a $-\dot{C}XY$ radical may be deduced from the fact that attack of a free radical Z (= CF_3, CCl_3, Br, etc.) on the olefins $CF_2{:}CXY$ (where X = F, Y = Cl; X = Y = Cl; X = F, Y = CF_3) yields $ZCF_2{\cdot}\dot{C}XY$ rather than the less stable radical $ZCFCl{\cdot}\dot{C}F_2$.[8] Trifluoronitrosomethane is particularly sensitive to radical attack, which takes place on nitrogen to give $Z{\cdot}N(CF_3){\cdot}O{\cdot}$ rather than $(CF_3)(ZO)N{\cdot}$.[9]

A similar argument based on diradical formation from trifluoronitrosomethane, $CF_2{\cdot}\dot{N}{\cdot}\dot{O}$, followed by attack of the more reactive of the species $-\dot{N}-$ or $-\dot{O}$, *i.e.*, the nitrogen radical, on the olefin, would lead to the same result:



Diradical formation from the olefin is somewhat favoured, since it also explains formation of cyclobutane compounds on dimerisation of fluoroethylenes of type $CF_2{:}CXY$:



where head-to-head addition greatly predominates.

The above schemes lead to the predominance of an oxazetidine in which the nitrogen is attached to the carbon of the original olefin $CF_2{:}CXY$ most readily attacked by a free radical. This gives a direction of addition in oxazetidine formation opposite to that involved in polymer formation. Polymer formation involves attack on the trifluoronitrosomethane in the 1 : 1 complex by a free radical from *outside* the complex—the initiating radical R·, or the growing polymer $R{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{\cdot}$. The new radical so formed $R{\cdot}N(CF_3){\cdot}O{\cdot}$ or $R{\cdot}N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CXY{\cdot}N(CF_3){\cdot}O{\cdot}$ then immediately attacks the CF_2 group of the nearby olefin $CF_2{:}CXY$ which had been present in the 1 : 1 complex.

Kinetic studies are in progress to throw further light on the mechanism of these novel reactions.

Experimental

Trifluoronitrosomethane was prepared by irradiation of a mixture of trifluoroiodomethane and nitric oxide in the presence of mercury. Chlorotrifluoroethylene and 1,1-dichlorodifluoroethylene were commercial samples purified by distillation with particular care to remove traces of peroxides. Hexafluoropropene was obtained by pyrolysis of anhydrous sodium heptafluorobutyrate and was purified by distillation *in vacuo*. All the olefins had correct molecular weights and were spectroscopically pure.

[9] Haszeldine and Steele, *J.*, 1957, 2800.

Products were identified by physical properties, by spectroscopic examination, by vapour-phase chromatography, and by determination of molecular weight (Regnault's method). Mixtures were analysed by infrared spectroscopy or by vapour-phase chromatography. Distillations were carried out in a vacuum-apparatus for manipulation of volatile compounds so that handling losses were usually negligible.

Reactions were carried out in sealed, evacuated Pyrex or silica tubes, filled by condensation from the vacuum-apparatus; air, moisture, etc., were thus excluded.

Reaction of Trifluoronitrosomethane with Chlorotrifluoroethylene.—The nitroso-compound (0·200 g., 2·0 mmole) and chlorotrifluoroethylene (0·233 g., 2·0 mmole) were sealed in a 40 ml. Pyrex tube and heated at 70° for 24 hr.; the blue colour had almost disappeared. Removal of the volatile products from the small amount of polymer (15% based on $CF_3{\cdot}NO$ used), and fractionation, gave unchanged reactants (15%) and *4-chloro-3,3,4-trifluoro-2-trifluoromethyl-1,2-oxazetidine* (0·309 g., 1·43 mmole; 85% based on $CF_3{\cdot}NO$ used) as a colourless liquid (Found: C, 16·4; N, 6·6%; *M*, 217. C_3ClF_6NO requires C, 16·6; N, 6·5%; *M*, 215·5), b. p. 30·0° (isoteniscope).

A similar reaction mixture kept at −45° (1 hr.), then allowed to warm to room temperature during 24 hr. and kept at room temperature for 6 days, yielded only 1% of the oxazetidine and mainly a very viscous colourless *copolymer* $[N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CFCl]_n$ (95% yield) (Found: C, 16·6; N, 6·7. C_3ClF_6NO requires C, 16·6; N, 6·5%).

Pyrolysis of the Oxazetidine $\overset{\frown}{N(CF_3){\cdot}O{\cdot}CFCl{\cdot}CF_2}$.—The oxazetidine (0·950 g., 4·42 mmole) was passed at 5 mm. pressure through a Pyrex tube (10 mm. internal diameter) heated to 450° over 7 cm. Air was excluded. The pyrolysis was repeated. The yellow products that had condensed in a trap cooled to −183° were shaken with mercury to remove chlorine and fractionated to give unchanged oxazetidine (2·75 mmole, 60%), perfluoro(methylenemethylamine) (1·65 mole, 99% yield based on the oxazetidine decomposed), carbonyl chlorofluoride, and carbonyl fluoride. Identification of the products was confirmed by infrared spectroscopic examination, which also showed that not even traces of the compound $CF_3{\cdot}N{:}CFCl$ had been formed. Under these pyrolysis conditions the compound COFCl is partly decomposed into COF_2 and $COCl_2$, which in turn affords carbon monoxide and chlorine.

Pyrolysis of the Polymer $[N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CFCl]_n$.—The polymer (2·01 g.) contained in a Pyrex tube, closed at one end and with the other end attached to a vacuum-pump *via* a trap cooled in liquid oxygen, was slowly inserted into a furnace at 550°. Some of the polymer (0·40 g., 20%) distilled into the cooler part of the tube. The volatile products were distilled to give *chlorofluoromethylenetrifluoromethylamine*, $CF_3{\cdot}N{:}CFCl$ (6·6 mmole, 88% yield based on polymer decomposed) (Found: C, 16·3; N, 9·2%; *M*, 149·6. C_2ClF_4N requires C, 16·1; N, 9·4%; *M*, 149·5), b. p. 5·5° (isoteniscope), carbonyl fluoride (90% yield based on polymer decomposed), perfluoro(methylenemethylamine) (<5% yield based on polymer decomposed), and silicon tetrafluoride.

Attempted Reaction of Chlorofluoromethylenetrifluoromethylamine with Carbonyl Fluoride.—The compound $CF_3{\cdot}N{:}CFCl$ (0·075 g., 0·50 mmole) and carbonyl fluoride (0·033 g., 0·50 mmole) were thoroughly mixed as gases in a 200-ml. trap fitted with a tap leading to a silica tube (15 mm. internal diameter) heated at 500° over 30 cm. and a receiving trap cooled in liquid oxygen. The tap was opened slightly so that the mixed gases passed through the heated tube into the receiver. This procedure was repeated. Fractionation gave unchanged chlorofluoromethylenetrifluoromethylamine (0·068 g., 0·45 mmole; 90%) and a mixture of carbonyl fluoride and silicon tetrafluoride (0·52 mmole). Infrared spectroscopic examination revealed no trace of the compounds $CF_3{\cdot}N{:}CF_2$, $COCl_2$, or COFCl.

Similar experiments were carried out with the compounds $CF_3{\cdot}N{:}CF_2$ and $COCl_2$, and $CF_3{\cdot}N{:}CCl_2$ and COF_2; halogen exchange was not detected.

Reaction of Trifluoronitrosomethane with 1,1-Dichlorodifluoroethylene.—(a) *At* 100°. Trifluoronitrosomethane (0·99 g., 10·0 mmole) and 1,1-dichlorodifluoroethylene (1·06 g., 7·9 mmole), sealed in a 100 ml. Pyrex tube and kept at 100° in the dark for 24 hr., gave unchanged nitroso-compound (0·23 g., 2·3 mmole), some polymer, and *4,4-dichlorodifluoro-2-trifluoromethyl-1,2-oxazetidine* (VII) (1·17 g., 65% based on nitroso-compound consumed) (Found: C, 15·8; N, 5·8%; *M*, 230. $C_3Cl_2F_5NO$ requires C, 15·5; N, 6·0%; *M*, 230), b. p. 63° (isoteniscope). (b) *At* 20°. Trifluoronitrosomethane (1·01 g., 10·2 mmole) and 1,1-dichlorodifluoroethylene (1·35 g., 10·2 mmole) were kept in a sealed 100 ml. Pyrex tube until the vapour phase was only

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faintly blue (5 days). Fractionation gave unchanged reactants (23%), the oxazetidine (0·058 g., 3%), and *the polymer* [·N(CF_3)·O·CF_2·CCl_2·]$_n$ (1·75 g., 97% based on nitroso-compound consumed) [Found: C, 15·9; N, 6·3%. ($C_3F_5Cl_2NO$)$_n$ requires C, 15·5; N, 6·0%] as a viscous liquid or elastomeric gel.

Reactions of the Oxazetidine (VII).—(a) *Attempted hydrolysis.* The oxazetidine (0·085 g.) was recovered unchanged after being heated with 10% aqueous sodium hydroxide (2 ml.) at 100° for 4 hr. The aqueous solution gave a weak test for chloride and fluoride ions, indicating that hydrolysis was taking place, but very slowly. (b) *Pyrolysis.* The oxazetidine (0·510 g., 2·20 mmole) was passed four times, at *ca.* 5 mm. pressure and in absence of air, through a silica tube (15 mm. internal diameter) heated at 400° over a 30 cm. length, the reaction products being condensed in traps cooled by liquid oxygen. Non-condensable gas (carbon monoxide) was formed. The pale yellow condensate was shaken with mercury to remove chlorine, then fractionated to give perfluoro(methylenemethylamine), CF_2·N:CF_2 (0·88 mmole, 98% based on oxazetidine consumed), unchanged oxazetidine, carbonyl chloride (0·24 mmole), and traces of the compounds CF_3·N:CCl_2, CF_2:CCl_2, COF_2, and CF_3NO.

Pyrolysis of the Polymer [·N(CF_3)·O·CF_2·CCl_2·]$_n$.—The polymer (2·35 g.), contained in a platinum tube closed at one end and attached through a trap cooled in liquid air to a vacuum pump, was heated to 550° *in vacuo*. Under these conditions, none of the polymer distilled unchanged to cooler parts of the tube. The blue condensate was distilled to give (i) *dichloromethylenetrifluoromethylamine*, CF_3·N:CCl_2 (82% based on polymer taken) (Found: C, 14·2; N, 8·1%; *M*, 170. $C_2NCl_2F_3$ requires C, 14·4; N, 8·1%; *M*, 166), as a colourless liquid, b. p. 47° (isoteniscope), (ii) carbonyl fluoride (79%), (iii) perfluoro(methylenemethylamine) (8%), (iv) carbonyl chloride (6%), (v) 1,1-dichlorodifluoroethylene (5%), and (vi) trifluoronitrosomethane (3%). The compound CF_3·N:CFCl was not detected.

Pyrolysis of the polymer in a silica tube at *ca.* 450° *in vacuo* gave similar products, though in lower yield (*e.g.*, CF_3·N:CCl_2 65%), since part of the polymer distilled unchanged and condensed in cooler parts of the apparatus. Carbon monoxide was also detected.

Reduction of Perfluoro(methylenemethylamine) with Hydrogen Chloride.—Perfluoro(methylenemethylamine) (1·01 g., 7·5 mmole), and anhydrous hydrogen chloride (0·288 g., 7·9 mmole) sealed in a 50 ml. Pyrex tube at 20° for 44 hr. gave (i) dichloromethylenetrifluoromethylamine, CF_3·N:CCl_2 (1·6 mmole, 26%) (Found: *M*, 164. Calc. for $C_2NF_3Cl_2$: *M*, 166), spectroscopically identical with the compound obtained by the pyrolysis of the polymer [·N(CF_3)·O·CF_2·CCl_2·]$_n$, (ii) bistrifluoromethylamine (4·1 mmole, 54%) (Found: *M*, 152. Calc. for C_2HNF_6: *M*, 153) identified by means of its infrared spectrum, and (iii) unchanged hydrogen chloride (Found: *M*, 39. Calc. for HCl: *M*, 36·5), (iv) a small amount of chlorofluoromethylenetrifluoromethylamine, CF_3·N:CFCl, spectroscopically identical with the compound obtained by the pyrolysis of the polymer [·N(CF_3)·O·CF_2·CFCl·]$_n$.

Reaction of Trifluoronitrosomethane with Hexafluoropropene.—The nitroso-compound (0·60 g., 6·7 mmole) and hexafluoropropene (1·00 g., 6·7 mmole) failed to react in an evacuated 50 ml. Pyrex tube at 70° during 120 hr. The blue colour disappeared when the tube was kept at 100° for 120 hr., and fractionation gave a mixture of carbon dioxide and silicon tetrafluoride (0·23 g.), a mixture of hexafluoropropene and trifluoronitromethane (1·26 g.; *M*, 139), and a fraction (0·05 g.; *M*, 225) spectroscopic examination of which revealed the characteristic oxazetidine absorption at 7·3 μ.

Increase in pressure facilitated the reaction. In a second experiment, trifluoronitrosomethane (4·24 g., 43 mmole) and hexafluoropropene (6·43 g., 43 mmole) were kept in a 30 ml. evacuated stainless steel autoclave (initial pressure 25—30 atm.) at 100° for 14 days. Fractionation gave (*a*) *perfluoro-2,4-bis(trifluoromethyl)-1,2-oxazetidine* (0·7 g., 7%) (Found: C, 19·0; N, 5·4%; *M*, 248. C_4F_9NO requires C, 19·3; N, 5·6%; *M*, 249) as a colourless liquid, b. p. (isoteniscope) 22·3°, (*b*) a small quantity (0·1 g., 1%) of a colourless liquid ($C_4F_9NO)_2$ (Found: C, 19·2; N, 5·8%; *M*, approx. 500) of vapour pressure approx. 20 mm. at 20°, and (*c*) *the polymer* [·N(CF_3)·O·CF_2·CF(CF_3)·]$_n$ (3·94 g., 35%) (Found: C, 19·2; N, 5·6. [C_4F_9NO]$_n$ requires C, 19·3; N, 5·6%) as a colourless heavy oil.

The vapour pressure of the oxazetidine determined over the range −7° to 16° is given by the equation $\log_{10} p$ (mm.) = 7·462 − 1353/*T*, whence the latent heat of vaporisation is 6190 cal./mole, and Trouton's constant is 21·0.

Pyrolysis of the Oxazetidine from Trifluoronitrosomethane and Hexafluoropropene.—The method is as described above. The oxazetidine (0·70 g., 2·8 mmole) was passed at 2—3 mm.

pressure during 20 min. through the pyrolysis tube at 550°. Distillation gave a fraction (0·29 g.) consisting of trifluoroacetyl fluoride (Found: *M*, 108. Calc. for C_2F_4O: *M*, 116) contaminated by small amounts of carbonyl fluoride and silicon tetrafluoride, and a fraction (0·40 g.) consisting of perfluoro(methylenemethylamine) (Found: *M*, 130. Calc. for C_2F_5N: *M*, 133), and small amounts of trifluoroacetyl fluoride and perfluoro(ethylidenemethylamine). Spectroscopic analysis showed that the pyrolysis products and yields were $CF_3{\cdot}N{:}CF_2$ 90%, $CF_3{\cdot}COF$ 90%, COF_2 10% and $CF_3{\cdot}N{:}CF{\cdot}CF_3$ 10%.

Pyrolysis of the Copolymer from Trifluoronitrosomethane and Hexafluoropropene.—The copolymer (0·868 g.), pyrolysed during 20 min. at 550° by the technique described earlier, gave perfluoro(ethylidenemethylamine), $CF_3{\cdot}N{:}CF{\cdot}CF_3$ (90% yield) (Found: C, 19·7; N, 7·3%; *M*, 183. C_3F_7N requires C, 19·7; N, 7·6%; *M*, 183), b. p. (isoteniscope) −15°, carbonyl fluoride (90% yield), trifluoroacetyl fluoride (10% yield), and perfluoro(methylenemethylamine) (10% yield). The vapour pressure of perfluoro(ethylidenemethylamine) is given by $\log_{10} p$ (mm.) = 7·221 − 1119/*T*, whence the latent heat of vaporisation is 5125 cal./mole and Trouton's constant 19·9.

Preparation of Perfluoro(methylene-ethylamine) $C_2F_5{\cdot}N{:}CF_2$.—Perfluoro-(2-ethyl-1,2-oxazetidine) (0·231 g., 0·94 mmole), prepared by interaction of pentafluoronitrosoethane and tetrafluoroethylene, was pyrolysed at 550° under 2—3 mm. pressure during 10 min., to give *perfluoro(methylene-ethylamine)* (0·168 g., 0·92 mmole) (Found: C, 19·6; N, 7·6%; *M*, 182. C_3F_7N requires C, 19·7; N, 7·6%; *M*, 183), b. p. (isoteniscope) −6°, and carbonyl fluoride (0·060 g., 0·92 mmole) (*M*, 66). The vapour pressure of perfluoro(methylene-ethylamine) is given by the equation $\log_{10} p$ (mm.) = 7·903 − 1341/*T*, whence the latent heat of vaporisation is 6110 cal./mole and Trouton's constant is 22·9.

Elastomer Formation from Trifluoronitrosomethane and Tetrafluoroethylene.—A series of reactions was carried out with highly pure trifluoronitrosomethane and tetrafluoroethylene. The reactants were sealed *in vacuo* in 5—10 mm. (internal diameter), thick-walled Pyrex or silica tubing capable of withstanding high pressures, and precautions were taken against explosions. The rate of reaction could be followed visually by disappearance of the blue colour. After removal of volatile products the polymer was examined to see if it was a mobile or viscous oil or an elastomer.

(a) *Reactant purity.* Experiments in which reactants were deliberately contaminated by addition of trifluoroiodomethane, trifluoronitromethane, dinitrogen tetroxide, nitric oxide, air, or moisture, then allowed to react under near-optimum conditions of temperature, pressure, etc., showed clearly that oily polymers were produced rather than the elastomer.

(b) *Reactant ratio.* No major difference could be detected in the rate of reaction, the yield of polymer, or the quality of the polymer, when molar reactant ratios between 0·8 : 1 and 1·5 : 1 were used. Use of 1 : 5, 1 : 10, 5 : 1, or 10 : 1 ratios gave only oils, but the oils were still exclusively 1 : 1 copolymers, *i.e.*, neither of the monomers was incorporated in the copolymer in excess of the 50% molar ratio.

(c) *Temperature.* Polymerisation occurred at −65°, −20°, 0°, 20°, 40°, or 100°. At 100°, the oxazetidine was the main product, and the polymer was always a mobile oil, never an elastomer. Elastomer of long chain-length was produced at −65°, but only slowly. No difference was detected in the rate of reaction at −20°, 0°, or 20°, but a trend could be detected towards elastomer of shorter chain-length as the reaction temperature increased, and at 40° a very viscous oil, almost a glass, was produced of molecular weight 80,000—100,000.

(d) *Pressure.* Increase in pressure increased the rate of reaction and the chain-length of the polymer. The pressures could not be measured, but could be calculated when liquid phase was absent. Increase in initial pressure from 1 to 20 atm. at −20° gave a distinct increase in rate of reaction and in quality of the elastomer. At an initial pressure calculated as 80 atm. the elastomer was formed within 30 min. and was hard and tough with good "snap." In all cases the rate of reaction appeared to increase as soon as an appreciable liquid phase was present.

(e) *Time.* This varied from 30 min. when high pressure was used, to 7 days for reaction at low temperature or pressure, or with impure reactants.

(f) *Optimum conditions.* Pure reactants with a molar ratio of 1 : 1, or close to it, at a temperature of 0° and a calculated pressure of 20 atm. produced elastomeric 1 : 1 copolymer of molecular weight 500,000—1,500,000 in 95% yield after 24 hr. in the dark on a 2 g. scale in sealed evacuated glass or silica vessels.

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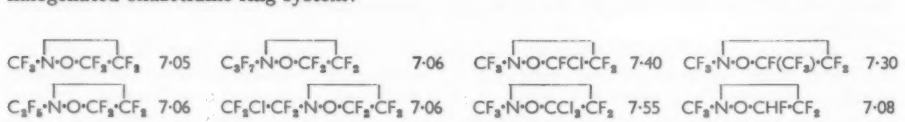
(g) *Conversion of oil into elastomer.* The oil could often be converted into the elastomer in two ways. The simplest was to heat the oil at 50—150° *in vacuo* for 1—7 days. Alternatively, the oil could be sealed with fresh trifluoronitrosomethane and tetrafluoroethylene and kept under near-optimum conditions; then the final polymer was an elastomer. The molecular weight of elastomer obtained by either procedure never exceeded 500,000.

(h) *Pyrolysis of the elastomer.* The elastomer (1·00 g.), pyrolysed at 550° by the technique described above, gave only perfluoro(methylenemethylamine) (98% yield) and carbonyl fluoride (96% yield) contaminated by a small amount of silicon tetrafluoride; trifluoronitrosomethane and tetrafluoroethylene were absent.

Characteristic Vibration of the Oxazetidine Ring.—The infrared spectra of the oxazetidines described in this and earlier papers show the groups N:O, NO_2, $N{:}\overset{+}{N}(O)\overset{-}{}$, ONO, ONO_2, C:C, C:N, etc., to be absent. A strong band at 7·0—7·5 μ appears to be characteristic of the perhalogenated oxazetidine ring system:



Reaction of Trifluoronitrosomethane with Nitric Oxide.—The nitroso-compound (0·125 g., 1·26 mmole), nitric oxide (0·60 g., 20 mmole), and mercury (10 ml.) in a sealed 85 ml. silica tube were allowed to warm from liquid-nitrogen temperature. Whilst liquid nitric oxide and nitroso-compound were still present a vigorous reaction ensued, and mercuric oxide began to coat the walls of the tube. Dinitrogen tetroxide caused the gas phase to change from blue to green, but the blue colour was regained later when the tube was shaken so that the mercury came into contact with the gas. After 5 min. the tube was opened and found to contain nitrogen, unchanged trifluoronitrosomethane (0·069 g., 0·70 mmole, 56%), trifluoronitromethane (0·040 g., 0·35 mmole, 63% based on CF_3·NO consumed), carbon dioxide (0·005 g., 0·10 mmole, 18% based on CF_3·NO consumed), and *O*-nitrosobistrifluoromethylhydroxylamine (0·010 g., 0·05 mmole, 18% based on CF_3·NO consumed).

When the reaction was repeated in absence of mercury, there was a similar vigorous decomposition at low temperature in the liquid phase, and the same products were obtained with the addition of dinitrogen tetroxide.

Thermal Decomposition of Trifluoronitrosomethane.—The nitroso-compound (150 ml. gas, 0·6 g.) was heated in a sealed 50 ml. Pyrex tube at 100° until the blue colour had disappeared (10 days). After a further 2 days the tube was opened and found to contain nitrogen, trifluoronitromethane (48% yield), carbon dioxide, and silicon tetrafluoride (40% yield).

The authors are indebted to Imperial Chemical Industries Limited, Plastics Division, for a grant (to D. A. B., 1953—1956).

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[*Received, May 18th,* 1960.]

261. *Polycyclic Cinnoline Derivatives. Part VI.*[1] *The Ultraviolet Absorption of Polycyclic Cinnolines and their* N*-Oxides.*

By J. F. Corbett, P. F. Holt, and A. N. Hughes.

The ultraviolet absorption spectra of seven unsubstituted polycyclic derivatives of cinnoline are recorded. The spectra resemble those of the carbocyclic analogues, except that the long-wavelength bands are at longer wavelengths and are more intense in the cinnoline spectra. The intensity increment is in good agreement with that predicted by Platt's "spectroscopic moment." An interesting relation between the wavelengths of the absorption bands and intramolecular overcrowding is observed. In non-polar solvents the cinnoline spectra have an additional absorption band which is ascribed to n–π^* transitions. *N*-Oxidation results in a bathochromic shift of the longer-wavelength absorption and an increase in the intensity of the long-wavelength band.

The polycyclic derivatives of cinnoline are of interest as heterocyclic analogues of the polycyclic aromatic hydrocarbons. Since each nitrogen atom contributes one electron to the π-electron system of the aromatic nucleus, the π-electron systems are similar to those of the carbocyclic analogues, and should therefore give rise to similar absorption spectra. Comparison of the spectra of the polycyclic cinnolines might, therefore, be expected to yield similar relationships to those found by comparison of the spectra of polycyclic aromatic hydrocarbons.

Badger and his collaborators [2,3] have shown that the ultraviolet absorption spectra of a number of polycyclic aza-hydrocarbons closely resemble those of their carbocyclic analogues, the main changes being a shift in the absorption to longer wavelengths, a loss of fine structure, and an increase in the intensity at longer wavelengths. Both the hydrocarbons and the aza-derivatives exhibit three main regions of absorption which have been designated,[2] in order of increasing wavelength, group I (log ε *ca.* 4·6), II (log ε *ca.* 4·0), and III (log ε *ca.* 3·2), these regions corresponding respectively to the β-, *p*-, and α-band of Clar's nomenclature.[4] The spectra of some aza-hydrocarbons in non-polar solvents also exhibit an additional absorption band at longer wavelengths (log ε *ca.* 2·6), which has been ascribed to n-π^* transitions.[5]

Comparison of the Spectra of Cinnolines and their Hydrocarbon Analogues.—Previous work on the spectra of polycyclic cinnolines has been confined to benzo[*c*]cinnoline [2,6,7] (I), substituted benzo[*c*]cinnolines,[7,8] and dibenzo[*c*,*f*]cinnoline [3,8] (II). We have redetermined the spectra of benzo[*c*]cinnoline and dibenzo[*c*,*f*]cinnoline, and measured the spectra of benzo[*f*]naphtho[2,1-*c*]cinnoline (III), dibenzo[*c*,*h*]cinnoline (IV), benzo[*h*]naphtho[1,2-*c*]-cinnoline (V), benzo[*f*]naphtho[1,2-*c*]cinnoline (VI), and tribenzo[*c*,*f*,*h*]cinnoline (VII), all in n-hexane solution. Comparison of the spectra with those of the corresponding aromatic hydrocarbons, as determined by Clar and Stewart,[9] shows that the introduction of two nitrogen atoms in place of two adjacent methine groups results in a bathochromic shift of the group II and III bands, a loss of fine structure, particularly in the group II band, and a considerable increase in the intensity of the group III band.

In studies of the spectra of benzene and its substituted derivatives the centres of the absorption bands are usually chosen for comparative purposes. In the higher polycyclic

[1] Part V, Corbett and Holt, *J.*, 1960, 3646.
[2] Badger, Pearce, and Pettit, *J.*, 1951, 3199.
[3] Badger and Walker, *J.*, 1956, 122.
[4] Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952.
[5] Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711; Badger and Walker, *J.*, 1956, 122.
[6] Calderbank and Le Fèvre, *J.*, 1948, 1949.
[7] Ramart-Lucas and Biquard, *Bull. Soc. chim. France*, 1936, 430.
[8] Ross and Kuntz, *J. Amer. Chem. Soc.*, 1952, **74**, 1297.
[9] Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235.

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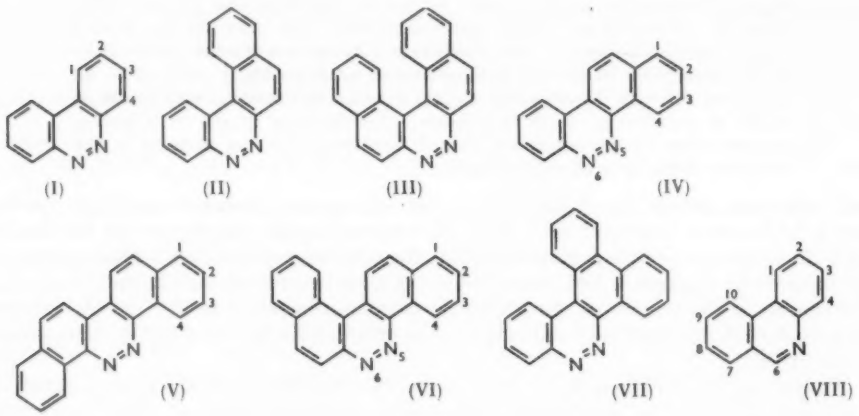
compounds the group II and III bands are partly masked by the previous, higher-intensity band, thus making the placing of the centre of these bands impossible. To obviate this difficulty, Platt,[10] in his theoretical treatment of the intensities of group III bands, chose the intensity of the smoothed curve at the wavelength of the longest-wavelength maximum in the band. We have chosen the wavelength of the longest wavelength maximum in each absorption band (called here λ_I, λ_{II}, and λ_{III}) for the purpose of evaluating shifts due to (*a*) the replacement of methine groups by nitrogen atoms and (*b*) nuclear annelation.



The bathochromic shifts of the group II band, resulting from the replacement of two methine groups by nitrogen atoms vary between 11 and 26 mμ, with the majority being about 11 mμ (Table 1). The shifts of the group III bands are between 10 and 17 mμ, except in the case of benzo[*h*]naphtho[1,2-*c*]cinnoline (V), for which the shift is only 2 mμ.

TABLE 1. *Values of* λ_I, λ_{II}, *and* λ_{III} *for polycyclic cinnolines (columns " a ") and their carbocyclic analogues (columns " b "). The shapes are obtained by joining the centres of the rings.*

		λ_I (mμ)			λ_{II} (mμ)			λ_{III} (mμ)		
Cpd.	Shape	a	b	(a − b)	a	b	(a − b)	a	b	(a − b)
I		250	*252*	−2	304	*293*	11	361	*346*	15
II		280	*281*	−1	327 s	*315*	12	387	*372*	15
III		304	*310*	−6	340 s	*329*	11	412	*395*	17
IV		272	*267*	5	330	*319*	11	371	*360*	11
V		284	*287*	−3	344 s	*329*	15	378	*376*	2
VI		297	*293*	4	347 s	*321*	26	396	*386*	10
VII		281	*286*	−5	345	*334*	11	383	*371*	12

s = shoulder.

Shifts of the group I band are small, less than 6 mμ, and are sometimes bathochromic and sometimes hypsochromic. It is interesting to compare these shifts with those of the corresponding phenanthridines, in which only one methine group is replaced by a

[10] Platt, *J. Chem. Phys.*, 1951, **19**, 263.

nitrogen atom. The spectra of phenanthridine [2] (VIII), benzo[*a*]phenanthridine,[11] benzo[*k*]phenanthridine,[11] benzo[*c*]phenanthridine,[12] and benzo[*i*]phenanthridine (all determined in ethanol) show very little shift of any of the three bands (Table 2).

The group III band in the spectra of the polycyclic aromatic hydrocarbons is attributed to a forbidden transition, and owes its intensity to vibrational interaction with stronger allowed transitions. The introduction of an aza-nitrogen atom in place of a methine group results in a perturbation leading to changes in the dipole moment during the transition, with a consequent increase in the intensity of absorption. According to the theory of Sklar,[13] Forster,[14] and Platt [10] the intensity increment, produced in the group III band of the spectrum of an aromatic hydrocarbon as a result of substitution, is

TABLE 2. *Values of* λ_I, λ_{II}, *and* λ_{III} *for some monoaza-hydrocarbons.*

Monoaza-hydrocarbon	Shape	λ_I	λ_{II}	λ_{III}
Phenanthridine [a]	⌐	250	296	343
Benzo[*k*]phenanthridine [b]	⟩	283	315 [d]	376
Benzo[*a*]phenanthridine [b]	⟩	278	314	375
Benzo[*c*]phenanthridine [c]	⌐	266	325	359
Benzo[*i*]phenanthridine [c]	⌐	262	320	359

[a] Badger, Pearce, and Pettit, *J.*, 1951, 3199; [b] Mills and Schofield, *J.*, 1956, 4213; [c] Badger and Seidler, *J.*, 1954, 2329; [d] shoulder.

proportional to a spectroscopic moment. Platt [10] gives a value of 38 for the spectroscopic moment of an aza-nitrogen atom, calculated as the square root of the observed intensity increment for pyridine and some of its substituted derivatives. Vector addition for 1,2-diaza-hydrocarbons predicts an intensity increment of 1444. The group III bands for phenanthrene and the higher polycyclic hydrocarbon analogues of the cinnolines under discussion have intensities between 125 and 400; it would thus be expected that the corresponding maxima in the cinnoline spectra would have intensities between 1550 and 1850 (*i.e.*, log ε *ca.* 3·2), which is found to be the case. The theory further predicts that the intensity increment for a mono-azahydrocarbon should be the same as for a 1,2-diaza-compound. The group III maxima of phenanthridine and the four benzophenanthridines referred to above have the predicted intensity (log ε *ca.* 3·2).

Effect of Nuclear Annelation of Benzo[c]*cinnoline.*—Nuclear annelation at the 1,2-bonds of benzo[*c*]cinnoline (I) produces analogues of the strained ring systems of benzo[*c*]phenanthrene and dibenzo[*c,g*]phenanthrene,[15] while annelation at the 3,4-bonds produces analogues of the unstrained chrysene and picene. The spectra of these two groups of cinnolines (Fig. 1) show differences in general shape, particularly in the group II band, which is well defined in the spectra of the unstrained cinnolines (I), (IV), and (V) but is a series of shoulders in the spectra of the strained systems (II) and (III). The spectra of benzo[*f*]naphtho[1,2-*c*]cinnoline (VI) and tribenzo[*c,f,h*]cinnoline (VII), in which only one of the additional rings produces ring strain, show well-defined group II bands.

Clar and Stewart [9] found that the ratio λ_I/λ_{III} in the spectra of the polycyclic aromatic hydrocarbons is related to the extent of strain in the ring system. The ratio λ_I/λ_{III} for the cinnolines shows no such relation, but a relation is evident for the ratios λ_I/λ_{II} and $\lambda_{II}/\lambda_{III}$ (Table 3). The former is 0·82 for the cinnolines free from ring strain, but increases as the extent of ring strain increases. The value for tribenzo[*c,f,h*]cinnoline (VII) is anomalous.

[11] Mills and Schofield, *J.*, 1956, 4213.
[12] Badger and Seidler, *J.*, 1954, 2329.
[13] Sklar, *J. Chem. Phys.*, 1942, **10**, 135.
[14] Forster, *Z. Naturforsch.*, 1947, **2a**, 149.
[15] Schmidt and Herbstein, *J.*, 1954, 3302; Johnson, *J. Org. Chem.*, 1959, **24**, 833; McIntosh, Robertson, and Vand, *J.*, 1954, 1661.

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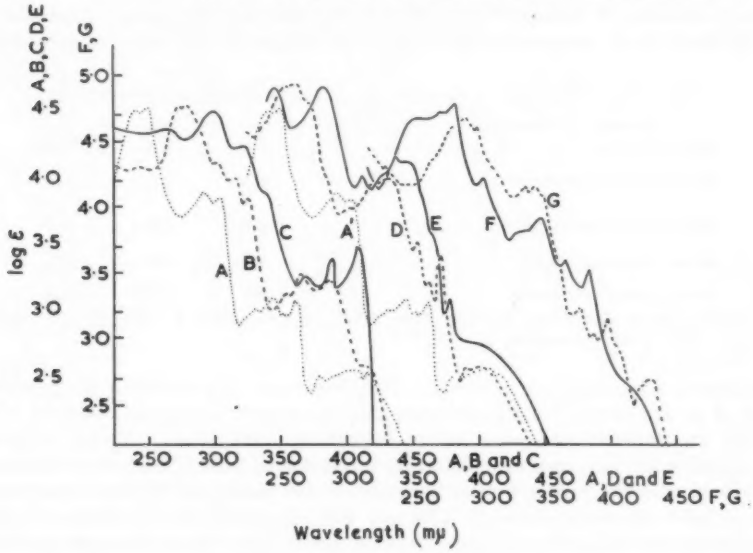
The ratio $\lambda_{II}/\lambda_{III}$ increases with increasing number of rings in the series of unstrained ring systems (I), (IV), and (V), but does not increase when the additional ring results in slight ring strain [see values for (I) and (II) and for (IV), (VI) and (VII)]. The value of this ratio for the highly strained system (III) is lower than that for any of the other cinnolines.

FIG. 1. *The absorption spectra of (A and A') benzo[c]cinnoline; (B) dibenzo[c,f]cinnoline; (C) benzo[f]-naphtho[2,1-c]cinnoline; (D) dibenzo[c,h]cinnoline; (E) benzo[h]naphtho[1,2-c]cinnoline; (F) tri-benzo[c,f,h]cinnoline; and (G) benzo[f]naphtho[1,2-c]cinnoline, all in n-hexane solution.*



The expected bathochromic shift of the group I and group III bands, with increase in the number of rings, which we shall call the " annelation shift," is greater for annelation at the 1,2-bond than for annelation at the 3,4-bond. The annelation shift of the group II band is independent of the position of annelation, and is about 26 mμ for one, and about

TABLE 3. *Ratios* λ_I/λ_{II}, $\lambda_{II}/\lambda_{III}$, *and* λ_I/λ_{I+I} *for some polycyclic cinnolines.*

Cinnoline	I	II	III	IV	V	VI	VII
Shape							
λ_I/λ_{II}	0·82	0·86	0·89	0·82	0·82	0·86	0·81
$\lambda_{II}/\lambda_{III}$	0·84	0·84	0·82	0·89	0·91	0·88	0·90
λ_I/λ_{III}	0·69	0·73	0·74	0·72	0·75	0·75	0·73

40 mμ for two added rings. Masking by the high-intensity group I bands thus accounts for the lack of definition of the group II bands in the spectra of (II) and (III).

The annelation shift of the group III band (Table 4) is about 9 mμ per additional ring for fusion at the 3,4-bond,and about 26 mμ at a 1,2-bond. The spectrum of benzo[*f*]-naphtho[1,2-*c*]cinnoline (VI) shows a shift of 35 mμ for λ_{III} compared with that of benzo[*c*]-cinnoline (I); this agrees with the expected value (9 + 26 mμ) for annelation at a 1,2- and a 3,4-bond. The low value of the shift for tribenzo[*c,f,h*]cinnoline (VII) may be due to the fact that both the additional rings are fused to the same ring. Comparison of λ_{III} for the benzophenanthridines with λ_{III} for phenanthridine (VIII) shows that the shifts are

greater for fusion at the 1,2- or the 9,10-bond than for fusion at the 3,4- or 7,8-bond (Table 4).

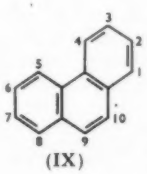
Comparison of λ_{III} for the higher polycyclic aromatic hydrocarbons with λ_{III} for phenanthrene (IX) shows a bathochromic shift of about 25 mμ per additional ring for annelation at the 1,2-bond, and of about 15 mμ per additional ring for annelation at a 3,4-bond

TABLE 4. *Annelation shifts (in* mμ*) of* λ_{III} *of the polycyclic cinnolines, hydrocarbons, and monoaza-hydrocarbons relative to* λ_{III} *for benzo*[c]*cinnoline, phenanthrene, and phenanthridine respectively.*

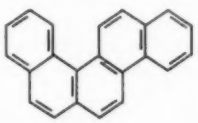
Shape						
Cinnoline	26	51	10	17	35	22
Hydrocarbon	26	49	14	30	40	25
Monoaza-hydrocarbon	28	—	11	—	—	—
	27	—	11	—	—	—

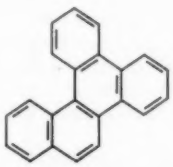
(Table 4). Benzo[*c*]chrysene (X) shows a shift for λ_{III} of 40 mμ, which agrees with the expected value (25 + 15 mμ) for annelation at both a 1,2- and a 3,4-bond. Benzo[*g*]chrysene (XI), the carbocyclic analogue of tribenzo[*c,f,h*]cinnoline (VII), exhibits a bathochromic shift of only 25 mμ, instead of the expected 40 mμ. The value of 332 mμ for λ_{III} of triphenylene (XII), which is derived by annelation of phenanthrene at the 9,10-bond, indicates that such annelation results in a *hypsochromic* shift of 14 mμ. Thus the low value for benzo[*g*]chrysene (XI) might be due to the presence of a triphenylene moiety in the molecule. A similar effect might account for the low value of λ_{III} for tribenzo[*c,f,h*]-cinnoline (VII).

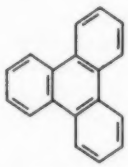
n-π* *Transitions.*—Badger and Walker [3] attributed the extra band in the spectrum of benzo[*c*]cinnoline (I) (at 410 mμ; log ε 2·6) in non-polar solvents, to an *n*-π* transition.



(IX)


(X)


(XI)


(XII)

The higher polycyclic cinnolines show similar absorption at longer wavelengths. Well-defined bands or shoulders of similar intensity (log ε *ca.* 2·6) occur at wavelengths between 400 and 430 mμ in the spectra of compounds (II), (IV), (V), (VI), and (VII), and are attributable to *n*-π* transitions. This feature is probably masked by the group III band in the spectrum of benzo[*f*]naphtho[2,1-*c*]cinnoline (III).

The spectra of benzo[*c*]cinnoline (I) and dibenzo[*c,f*]cinnoline (II) in ethanol show no fine structure and no *n*-π* transition.[3] This is true also for the spectra of dibenzo[*c,h*]-cinnoline (IV) and of benzo[*f*]naphtho[1,2-*c*]cinnoline (VI) in ethanol. Solvent–solute interaction, involving hydrogen bonding to the aza-nitrogen atoms, would increase the energy of the *n*-π* transition and result in an hypsochromic shift of the band which would then be masked by the group III band.

Effect of N-*Oxidation on Spectra.*—Calderbank and Le Fèvre,[6] comparing the spectra of benzo[*c*]cinnoline (I) and its *N*-oxide in ethanol, found that *N*-oxidation resulted in a bathochromic shift of the group II and III bands of about 30 mμ. We compared the spectrum of benzo[*c*]cinnoline (I) and its *N*-oxide in n-hexane (Fig. 2), and found that the shift of the group II band is 38 mμ, and that of the group III band is 21 mμ. In addition,

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the intensity of the group III band is considerably increased and the group I band is broadened to longer wavelengths. This broadening is also evident in the spectrum of the ethanolic solution, but it is resolved into two additional peaks, at 286 and 296 mμ, in n-hexane. Comparison of the spectrum of benzo[*c*]cinnoline *N*-oxide in n-hexane and in ethanol (Fig. 2) shows that while solvent–solute interaction has resulted in some loss of fine structure, the change is much less than that for benzo[*c*]cinnoline (I).[3]

FIG. 2.

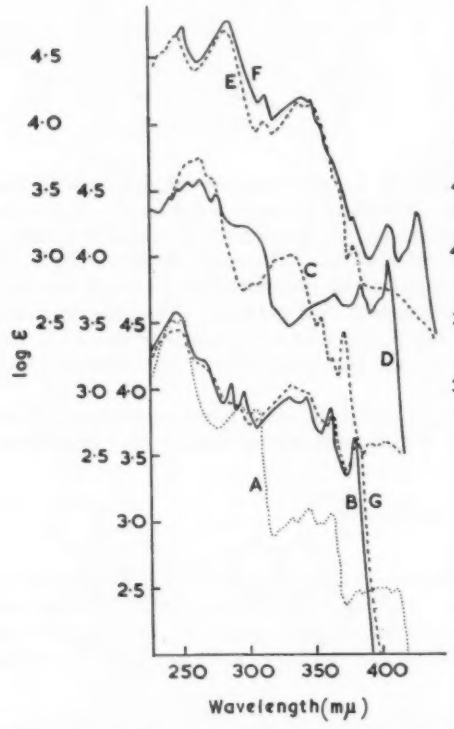

FIG. 3.

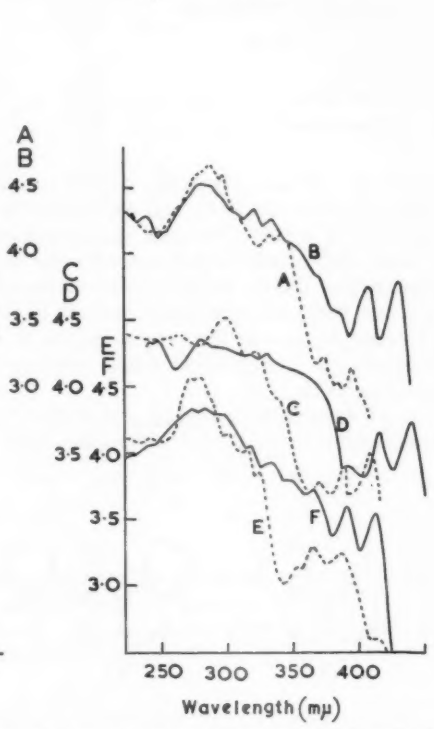

FIG. 2. *Absorption spectra of* (A) *benzo*[c]*cinnoline*; (B) *benzo*[c]*cinnoline* N-*oxide*; (C) *dibenzo*[c,h]-*cinnoline*; (D) *dibenzo*[c,h]*cinnoline* 6-*oxide*; (E) *benzo*[h]*naphtho*[1,2-c]*cinnoline*; *and* (F) *benzo*[h]-*naphtho*[1,2-c]*cinnoline* N-*oxide*, *in n-hexane solution, and of benzo*[c]*cinnoline* N-*oxide* (G) *in ethanol.*

FIG. 3. *Absorption spectra of* (A) *benzo*[f]*naphtho*[1,2-c]*cinnoline*, (B) *benzo*[f]*naphtho*[1,2-c]*cinnoline* 6-*oxide*, (C) *benzo*[f]*naphtho*[2,1-c]*cinnoline*, (D) *benzo*[f]*naphtho*[2,1-c]*cinnoline* N-*oxide*, (E) *dibenzo*-[c,f]*cinnoline*, (F) *dibenzo*[c,f]*cinnoline* N-*oxide*, *all in n-hexane.*

Figs. 2 and 3 compare the spectra of five higher polycyclic cinnolines with those of their *N*-oxides. The change in the spectrum of dibenzo[*c,h*]cinnoline (IV) on *N*-oxidation (Fig. 2) is similar to that for benzo[*c*]cinnoline, except that the bathochromic shifts of the group II and III bands are 32 and 34 mμ respectively, and that the broadening of the group I band is in the form of a shoulder. In the spectra of the *N*-oxides of dibenzo[*c,f*]-cinnoline (II), benzo[*f*] naphtho[2,1-*c*]cinnoline (III) and benzo[*f*]naphtho[1,2-*c*]cinnoline (VI), the broadening of the group I band has caused the group I and II bands to merge, with the production of a broad absorption region between 250 and 370 mμ (Fig. 3). As before, the bathochromic shift of the group III band [28 mμ for (III), 27 mμ for (II), and 36 mμ for (VI)] is accompanied by a large increase in the intensity.

The effect of *N*-oxidation on the spectrum of benzo[*h*]naphtho[1,2-*c*]cinnoline (V) (Fig. 2) differs, in some respects, from its effect on the spectra of other cinnolines. While there is a large bathochromic shift (48 mμ) of the group III band, the increase in its intensity is less marked, and the group I and group II bands are not altered appreciably. This abnormality may be ascribed to intramolecular overcrowding between the oxygen atom and the 4-hydrogen atom, resulting in the bending of the N–O bond out of the plane of the ring system, thus reducing the interaction of the unshared electrons of the oxygen atom with the π-electron system of the nucleus. This contrast supports our earler suggestion,[16] that the *N*-oxides of dibenzo[*c*,*h*]cinnoline (IV) and of benzo[*f*]naphtho[1,2-*c*]cinnoline (VI) are the 6-oxides.

Conclusion.—The generalisations which appear from this series of spectra may be summarised as follows. The spectra of polycyclic cinnolines resemble, in form, those of their carbocyclic analogues, but the group II and III bands are shifted to longer wavelengths, the shifts being considerably greater than those of the corresponding monoazahydrocarbons.

There appears to be a relation between the features of the spectra and the position of annelation of benzo[*c*]cinnoline (I) and the extent of ring strain resulting from intramolecular overcrowding. Thus annelation at the 1,2-bond produces a much larger bathochromic shift of the group I and II bands than does annelation at the 3,4-bond. The ratio $\lambda_{II}/\lambda_{III}$ increases with increasing number of rings only if the additional rings do not result in ring strain. The ratio λ_{I}/λ_{II} is constant for molecules in which there is no strain but increases with the extent of ring strain.

N-Oxidation results in an increase in intensity and a bathochromic shift of the group III band.

Experimental.—Cinnolines and cinnoline N*-oxides.* Benzo[*c*]cinnoline was prepared by the method of Badger *et al.*[17] and benzo[*c*]cinnoline *N*-oxide by that of King and King.[18] The preparation of dibenzo[*c*,*f*]cinnoline, dibenzo[*c*,*h*]cinnoline, and benzo[*f*]naphtho[1,2-*c*]cinnoline,[16] and of benzo[*f*]naphtho[2,1-*c*]cinnoline and benzo[*h*]naphtho[1,2-*c*]cinnoline [19] and their *N*-oxides has been described previously, as has the preparation of tribenzo[*c*,*f*,*h*]cinnoline.[20] All materials were purified by chromatography on alumina in benzene–light petroleum.

Solvents.—Ethanol and n-hexane were B.D.H. special spectrophotometric grade.

Spectra.—The spectra were determined by using a Unicam 500 spectrophotometer.

The authors acknowledge the loan of a spectrophotometer by the Royal Society and one (A. N. H.) a maintenance grant from Imperial Chemical Industries Limited, Paints Division.

THE UNIVERSITY, READING. [*Received, June 1st,* 1960.]

[16] Corbett and Holt, *J.*, 1960, 3646.
[17] Badger, Seidler, and Thomson, *J.*, 1951, 3207.
[18] King and King, *J.*, 1945, 824.
[19] Braithwaite and Holt, *J.*, 1959, 3025.
[20] Corbett, Holt, and Hughes, *J.*, 1960, 3643.

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262. *Infrared Absorption Spectra of Aliphatic Nitro-alcohols. Part I. Spectra of Monohydric Nitro-alcohols and their Chloro- and Bromo-derivatives.*

By Z. Eckstein, P. Gluziński, W. Sobótka, and T. Urbański.

Infrared absorption spectra of aliphatic nitro-alcohols and their chloro- and bromo-derivatives have been measured. The length of the carbon chain does not appreciably influence the frequency of NO_2 bands.

Replacement of hydrogen atoms attached to $C_{(1)}$ by one or two chlorine atoms increases (by 14—21 and 30 cm.$^{-1}$ respectively) the frequency of asymmetric NO_2 vibrations and lowers the frequency of symmetric vibrations (17—32 and 50 cm.$^{-1}$ respectively). A similar effect is produced by bromine but the increase of the frequency of asymmetric vibrations is much smaller (5—16 cm.$^{-1}$).

A band at 1424—1416 cm.$^{-1}$ in the spectra of compounds with a primary nitro-group is probably due to scissors vibrations of C–H in $CH_2 \cdot NO_2$. Assignments are also made for some other bands.

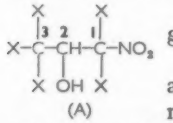
Little has been published so far on infrared absorption spectra of aliphatic nitro-compounds. Nevertheless a conclusion can be drawn that both asymmetric and symmetric vibrations of the nitro-group are subject to shift under the influence of some functional groups attached to the alkyl chain. For instance, Haszeldine [1] found that chlorine, in a few chloronitro-alkanes, has a strong influence on the frequencies of the nitro-group. Brown,[2] and Luther and Günzler,[3] came to a similar conclusion. Urbański and his colleagues [4] examined ultraviolet absorption spectra of halogen derivatives of nitro-alcohols and stated that the intensities of the absorption maxima characterising nitro-group are considerably reduced by halogen atoms.

In the present paper we examined the effects, on the infrared frequencies of the nitro-group of aliphatic β-nitro-alcohols, of the chain length of an alkyl group attached to $C_{(3)}$ (formula A), and of chlorine or bromine in various positions.

The nitro-alcohols, all obtained by known methods, are listed in Table 1. The infrared absorption bands are reported in Table 2.

Nitro-group Stretching Vibrations.—The asymmetric frequencies of the nitro-group are not influenced by the length of the carbon chain (C_2—C_{11}) to which the nitro-group is attached. The length of the carbon chain has a slight influence on the symmetric vibrations: thus the first member (I) has a lower frequency than the others and there is a tendency for lowering of the frequency as the series is ascended.

The presence of chlorine and bromine produces a very strong influence on the character and frequency of the nitro- and hydroxyl absorption. The position of halogen with respect to the nitro-group is most important.



(A)

The asymmetric and the symmetric stretching vibrations of the nitro-group of our compounds (A) are listed in Table 3.

Asymmetric vibrations bands are in all cases very strong: for primary and the secondary nitro-compounds they are at 1554—1550 and 1545 cm.$^{-1}$ respectively [the only deviation is for 1-nitromethylcyclohexanol (XXXI) which give the frequency 1545 cm.$^{-1}$ although it is the primary nitro-compound].

Introduction of chlorine atom at position 1 strongly increases (by 14—21 cm.$^{-1}$) the frequency of the asymmetric vibrations. The influence of a bromine atom is less prominent (5—16 cm.$^{-1}$). Replacement of both active hydrogen atoms was examined for compounds

[1] Haszeldine, *J.*, 1953, 2526.
[2] Brown, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 6341.
[3] Luther and Günzler, *Z. Naturforsch.*, 1955, **10b**, 445.
[4] Sobótka, Urbański, and Eckstein, *Bull. Acad. Polon. Sci., Cl. III*, 1955, **3**, 441; Urbański, Sobótka, and Eckstein, *ibid.*, 1957, **5**, 209; Sobótka, Eckstein, and Urbański, *ibid.*, 1957, **5**, 653.

(IV—VI): the shift of the asymmetric frequency is 30, 25, and 15 cm.$^{-1}$ respectively, chlorine having a notably greater effect than bromine. The weaker influence of bromine is probably due to its lower electronegativity and seems to confirm the hypothesis [4,5] about the different influence of substitution by chlorine and bromine on the electronic spectrum of aliphatic nitro-alcohols.

No marked change of asymmetric frequency occurs when the position 3 is substituted by chlorine in derivatives of 1-nitropropan-2-ol (X—XIV), 1-methyl-1-nitropropan-2-ol

TABLE 1. *Physical properties of substances* HO·CHR·CXX'·NO_2.

No.	R	X	X'	B. p. °C	mm.	d_{20}^{20}	n_D^{20}	$[M]_D$ calc.	$[M]_D$ exper.
I	H	H	H	92—94	6	1·2975	1·4403	18·55	18·51
II	H	H	Cl	90	4—5	1·4934	1·4699	23·77	23·44
III	H	H	Br	101—102	5	1·9201	1·5020	26·67	26·13
IV	H	Cl	Cl	65—66	1·0	1·5824	1·4743	28·58	28·43
V	H	Cl	Br	70—71	0·8	1·9014	1·5044	31·48	31·85
VI	H	Br	Br	87	1·2	2·2521	1·5441	34·38	34·88
VII	Me	H	H	72·5—73	0·5	1·1906	1·4383	23·29	23·16
VIII	Me	H	Cl	71	0·6	1·3645	1·4603	28·06	27·93
IX	Me	H	Br	90—90·5	1·7	1·7485	1·4930	30·93	30·57
X	CH_2Cl	H	H	101—103	6	1·4234	1·4838	28·01	28·03
XI	$CHCl_2$	H	H	105	5	1·5691	1·5026	32·82	32·75
XII	CCl_3	H	H [a]	—	—	—	—	—	—
XIII	CCl_3	H	Cl	103—104	0·7	1·7081	1·5146	42·67	42·84
XIV	CCl_3	H	Br	104—106	0·8	1·9834	1·5361	45·56	45·17
XV	Me	H	Me	70—73	0·5	1·1353	1·4431	27·80	27·81
XVI	CH_2Cl	H	Me	102—103	3	1·3393	1·4781	32·63	32·45
XVII	$CHCl_2$	H	Me	113	2	1·4843	1·4971	37·45	37·00
XVIII	CCl_3	H	Me	109—110	2	1·5493	1·5032	42·26	42·40
XIX	Et	H	H	82·5	1·2	1·1353	1·4435	28·00	27·90
XX	Et	H	Cl	89	2	1·2793	1·4600	32·77	32·85
XXI	Et	H	Br	94—95	1	1·5941	1·4860	35·67	35·65
XXII	Pr^n	H	H	80—81	0·6	1·0908	1·4439	32·71	32·39
XXIII	Pr^n	H	Cl	87	1	1·2286	1·4575	37·48	37·18
XXIV	Pr^n	H	Br [b]	98—100	1	1·5222 [a]	1·4823 [a]	40·38	39·73 [a]
XXV	CH_3·CHCl·CCl_3	H	H	145	0·5	1·5111	1·5122	46·90	46·85
XXVI	Bu^n	H	H	103	2·5	1·0576	1·4482	37·11	37·26
XXVII	Bu^i	H	H	90	1·1	1·0587	1·4474	37·23	37·14
XVIII	Bu^i	H	Cl	79	0·5	1·1852	1·4586	41·85	41·83
XXIX	Bu^i	H	Br	107—108	1·2	1·4386	1·4837	44·79	44·93
XXX	n-C_5H_{11}	H	H	113	1·5	1·0306	1·4495	41·76	41·99
XXXI	$C_6H_{10}(OH)$·CH_2·NO_2			93	0·4	1·1616	1·4881	40·02	39·47
XXXII	$C_6H_{10}(OH)$·CHCl·NO_2			96·5	0·4	1·2907	1·5000	44·80	44·09
XXXIII	$C_6H_{10}(OH)$·CHBr·NO_2			118	1·0	1·5476	1·5208	47·70	46·80
XXIV	n-C_6H_{13}	H	H	115—118	1·5	1·0095	1·4499	46·41	46·63
XXXV	C_6H_{11}	H	H	123	1·0	1·1194	1·4880	44·64	44·52
XXXVI	C_6H_{11}	H	Cl	118	1·2	1·2365	1·4952	49·41	48·83
XXXVII	C_6H_{11}	H	Br	132	1·5	1·4764	1·5160	52·32	51·55
XXXVIII	n-C_7H_{15}	H	H	128	1·5	0·9966	1·4526	51·06	51·20
XXXIX	n-C_8H_{17}	H	H	126—128	1·0	0·9931	1·4550	55·70	55·53
XL	n-C_9H_{19}	H	H	142	1·5	0·9674	1·4549	60·35	60·9

[a] Examined as a supercooled liquid. [b] M. p. 45°. [c] M. p. 35°.

(XVI—XVIII), or 1-nitropentan-2-ol (XXV). The shift (1—6 cm.$^{-1}$) was near the experimental error.

Assignment of bands of symmetric vibrations of NO_2 was much more difficult: a number of bands have both frequencies and intensities similar to that expected and this is particularly true for our chloro-derivatives; a similar difficulty we described in our earlier papers.[6,7] We base our assignment on comparison of the spectra of nitro-alcohols and halogenonitro-alcohols with those of nitroalkanes and halogenonitroalkanes having chains

[5] Urbański, Eckstein, and Sobótka, *Roczniki Chem.*, 1955, **29**, 399; Eckstein, *ibid.*, 1956, **30**, 1151.
[6] Eckstein, Fluksik, and Sobótka, *Bull. Acad. Polon. Sci., Sér. chim., géol., géograph.*, 1959, **7**, 803.
[7] Eckstein, Gluziński, Hofman, and Urbański, *J.*, 1961, 489.

XUM

of same length and structure of carbon chain: for these, as we shall detail elsewhere,[8] the frequencies symmetric NO_2 vibrations are the same within experimental error (~3 cm.$^{-1}$). For instance, the spectrum of 1-chloro-1-nitropropane-2-ol (VIII) has strong bands at 1384 and 1367 cm.$^{-1}$; the spectrum of 1-chloro-1-nitropropane has a strong band 1364 cm.$^{-1}$, indicating the second of the above values as corresponding to symmetric NO_2 vibrations.

TABLE 2. *Some frequencies in the infrared absorption spectra.*

No.	Band frequencies (cm.$^{-1}$)
I	3551—3415m(b), 1554vs, 1421m, 1375s
II	3552—3405m(b), 3011m, 1571vs, 1353s
III	3539—3390m(b), 3023w, 1566vs, 1353m
IV	3533—3406s(b), 1584vs, 1325s, 899s, 847s
V	3532—3397m(b), 1579vs, 1324s
VI	3554—3430m(b), 1569vs, 1323s
VII	3538—3418s(b), 1552vs, 1423s, 1386s
VIII	3541—3427s(b), 1570vs, 1384s, 1367s, 1335w
IX	3535—3425m(b), 1566vs, 1365s
X	3537—3440m(b), 3026vw, 1553vs, 1423m, 1384s
XI	3534m(b), 3006vw, 1555vs, 1418m, 1379s, 790s
XII *	3525s(b), 3028w, 1558vs, 1419s, 1377s, 807vs
XIII	3518s(b), 3006w, 1579vs, 1355s, 822s, 803s
XIV	3509m(b), 3006w, 1566vs, 1353s, 825s
XV	3539—3452m(b), 1545vs, 1389s, 1361m
XVI	3531—3433m(b), 3004m, 1549vs, 1391m, 1362m
XVII	3526s(b), 3003m, 1549vs, 1391s, 1362s, 783s
XVIII	3526m(b), 3004vw, 1549vs, 1390m, 1357s, 824s, 797s
XIX	3543—3428s(b), 1553vs, 1421s, 1385s
XX	3538—3443s(b), 1572vs, 1368s, 1350s, 1331s
XXI	3545—3453s(b), 1565vs, 1366s
XXII	3549—3444s(b), 1553vs, 1424s, 1385s
XXIII	3530—3414m(b), 1570vs, 1370m, 1355m
XXIV *	3541—3447m(b), 1563vs, 1356s
XXV	3529m(b), 3039vw, 1556vs, 1417m, 1382s, 812s
XXVI	3535—3456m(b), 1551vs, 1418m, 1381s
XXVII	3538—3436s(b), 1552vs, 1422s, 1385s
XXVIII	3544—3442m(b), 1566vs, 1368s, 1353s
XXIX	3534—3435m(b), 1557vs, 1353s
XXX	3541—3449m(b), 1550vs, 1417m, 1381s
XXXI	3524—3448m(b), 1545vs, 1422sh, 1382s
XXXII	3538—3483m(b), 1562vs, 1353s
XXXIII	3537—3449m(b), 1556vs, 1350s
XXXIV	3541—3454m(b), 1550vs, 1417m, 1381s
XXXV	3522—3416m(b), 1550vs, 1419m, 1384s
XXXVI	3545—3476m(b), 1571vs, 1366m
XXXVII	3551—3457m(b), 1566vs, 1356m
XXXVIII	3534—3443m(b), 1551vs, 1416m, 1378s
XXXIX	3537—3438m(b), 1551vs, 1417m, 1377s
XL	3541—3451m(b), 1550vs, 1418m, 1379s

* Measurements of supercooled liquid.

We could not confirm the frequency 1340 cm.$^{-1}$ assigned by Haszeldine [1] for 1-chloro-1-nitropropane as we found only a weak band 1335 cm.$^{-1}$ in this compound which could not be assigned to the frequency in question. Similarly, 1-chloro-1-nitropentan-2-ol (XXIII) has bands at 1370 and 1355 cm.$^{-1}$, and the second was chosen as it is identical with the frequency of symmetric NO_2 vibrations of 1-chloro-1-nitropentane (1355 cm.$^{-1}$).

Comparison of the spectrum of a nitro-alcohol with that of the corresponding nitroparaffin does not always give a simple solution. 1-Chloro-1-nitrobutan-2-ol (XX) gives bands of almost identical intensity (strong) at 1368, 1350, and 1331 cm.$^{-1}$. The 1-chloro-1-nitrobutane gives a strong band at 1355 with a shoulder 1367 cm.$^{-1}$. Eventually we assigned the band 1368 cm.$^{-1}$ to symmetric NO_2 vibrations.

Broadly speaking, no general method of identification of bands of symmetric NO_2 vibrations exists, and the assignment is not always certain. The assignments made are

[8] Urbański, Eckstein, Sobótka, and Gluziński, unpublished work.

recorded in Table 3. The shift due to chlorine and bromine atom in the position 1 is in the direction of lower frequency, *i.e.*, in the opposite direction to that for asymmetric vibrations. The lowering is relatively strong and amounts to 17—32 cm.$^{-1}$. No difference between the action of chlorine and bromine was noticed, except for the derivatives of cyclohexylnitroethanol (XXXVI and XXXVII respectively) where the bromo-compound had a frequency lower by 10 cm.$^{-1}$.

TABLE 3. *Comparison of frequencies of the nitro-group in nitro-alcohols and their halogen* (Cl *and* Br) *derivatives.*

No.	Compound *	$\nu(NO_2)$ (cm.$^{-1}$) asymm.	symm.	No.	Compound *	$\nu(NO_2)$ (cm.$^{-1}$) asymm.	symm.
I	$HO{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2$	1554	1375	II	$HO{\cdot}CH_2{\cdot}CHCl{\cdot}NO_2$	1571	1353
				III	$HO{\cdot}CH_2{\cdot}CHBr{\cdot}NO_2$	1566	1353
				IV	$HO{\cdot}CH_2{\cdot}CCl_2{\cdot}NO_2$	1584	1325
				V	$HO{\cdot}CH_2{\cdot}CBrCl{\cdot}NO_2$	1579	1324
				VI	$HO{\cdot}CH_2{\cdot}CBr_2{\cdot}NO_2$	1569	1323
VII	$CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1552	1386	VIII	$CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1570	1367
				IX	$CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1566	1365
				X	$CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1553	1384
				XI	$CHCl_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1555	1379
				XII †	$CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1558	1377
				XIII	$CCl_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1579	1355
				XIV	$CCl_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1566	1358
XV	$CH_2{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1545	1361	XVI	$CH_2Cl{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1549	1364
				XVII	$CHCl_2{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1549	1362
				XVIII	$CCl_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1549	1357
XIX	$CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1553	1385	XX	$CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1572	1368
				XXI	$CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1565	1366
XXII	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1553	1385	XXIII	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1570	1355
				XXIV †	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1563	1356
				XXV	$CH_2{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1556	1382
XXVII	$Me_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1552	1385	XXVIII	$Me_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1566	1353
				XXIX	$Me_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1557	1353
XXXI	$C_6H_{10}(OH){\cdot}CH_2{\cdot}NO_2$	1545	1382	XXXII	$C_6H_{10}(OH){\cdot}CHCl{\cdot}NO_2$	1562	1353
				XXXIII	$C_6H_{10}(OH){\cdot}CHBr{\cdot}NO_2$	1556	1350
XXXV	$C_6H_{11}{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1550	1384	XXXVI	$C_6H_{11}{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1571	1366
				XXXVII	$C_6H_{11}{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1566	1356

* C_6H_{10} denotes cyclohexylidene. † Measurements of a supercooled liquid.

Two halogen atoms (IV—VI) produce a greater shift (50—52 cm.$^{-1}$), the same for chlorine as for bromine.

When chlorine atoms were introduced at position 3 only an insignificant shifting of symmetric vibrations (−3 to −9 cm.$^{-1}$) was observed. Replacement at position 1 and 3 (XIII, XIV) had a considerably greater effect.

The observed shifts of the bands of the nitro-group are in agreement with the findings by Haszeldine [1] and Brown [2] for the chlorine and bromine derivatives of nitroparaffins.

It seems to us that the shifts of the NO_2 frequencies can be explained (at least partly) by the fact that replacement at position 1 changes the nature of the nitro-compound. It is known that both bands of NO_2 vibrations for aliphatic secondary nitro-compounds are at lower frequencies than are those of aliphatic primary nitro-compounds. One halogen atom at position 1 produces a secondary nitro-compound and the final result is composed of two superposed partial effects, (1) that of the halogen, and (2) that of the nature of the nitro-group. For asymmetric NO_2 vibrations the effect (1) produces a shift to higher and effect (2) to lower frequencies; a higher frequency results which denotes the greater power of effect (1). For symmetric NO_2 vibrations both effects are in the same direction and a relatively large lowering of the frequency results.

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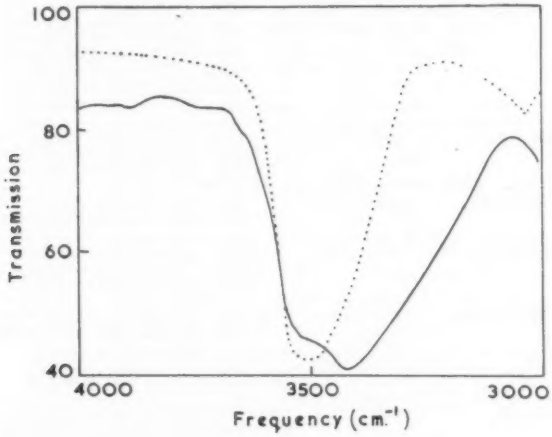
Hydroxyl Group.—All our nitro-alcohols give an absorption band between 3554 and 3390 cm.$^{-1}$ characterising the O–H stretching vibration. This band is broad and of middle intensity, indicating intermolecular hydrogen bonds. Two maxima (3554—3509 and 3483—3390 cm.$^{-1}$; full line in Figure) are observed. When two or three atoms of chlorine are attached at position 3 the second maximum disappears and the band becomes narrower (dotted line): this may signify that one type of hydrogen bond disappears for these compounds.

It should also be pointed out that the acidity of the hydroxyl groups is greater for the 3-trichloro-derivatives. This can be deduced by analogy with trichloroethanol: it may have a bearing on the ability to form hydrogen bonds.

Band at 3039—3003 *cm.*$^{-1}$.—A weak band at 3039—3003 cm.$^{-1}$ was noticed for all the halogenonitro-alcohols containing one or more halogen atoms at position 3. This band is

O–H *stretching vibrations of* 1-*nitropropan*-2-*ol* (*full line*) *and* 1,1-*dichloro*-3-*nitropropan*-2-*ol* (*dotted line*).



not present for unsubstituted nitro-alcohols and present only for some substituted products, such as 2-chloro- and 2-bromo-2-nitroethanol (II and III). Plyler and Benedict [9] found a similar band in the spectra of alkyl chlorides. It may be due to some C–H vibrations.

Band at 1424—1416 *cm.*$^{-1}$.—This band was found in all our nitro-alcohols containing primary nitro-groups. It is of high or medium intensity. Similar bands were reported by Brown.[2] They are probably produced by the scissors vibrations of the C–H bonds in the $CH_2 \cdot NO_2$ group. Urbański [10] reported bands of frequencies 4167 and 3704 cm.$^{-1}$ for similar nitro-alcohols and these are probably overtones of the band in question.

Band at 1391—1389 *cm.*$^{-1}$.—A strong band of this frequency was found in the spectra of all the nitro-alcohols with a system $CH_3 \cdot C \cdot NO_2$ (XV—XVIII), also by Brown,[2] according to whom it is due to deformation vibrations of C–H bonds in the methyl group attached to $C \cdot NO_2$.

Bands at 825—783 *cm.*$^{-1}$.—Strong and very strong bands 825—783 cm.$^{-1}$ are present in the spectra of all the nitro-alcohols containing two and three chlorine atoms at position 3 (XII—XIV, XVII—XVIII, XXV). They are probably formed by the vibrations of the groups CCl_2 and CCl_3. However the literature [11] reports lower frequencies (780—710 cm.$^{-1}$).

[9] Plyler and Benedict, *J. Res. Nat. Bur. Standards*, 1951, **47**, 202.
[10] Urbański, *Bull. Acad. Polon. Sci., Cl. III*, 1956, **4**, 87; 1956, **4**, 381; *Roczniki Chem.*, 1957, **31**, 37.
[11] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

Also strong bands at 899 and 847 cm.$^{-1}$ in the spectrum of 2,2-dichloro-2-nitroethanol (IV) may be assigned to CCl_2 and their shift to higher frequency may be due to the presence of the NO_2 group attached to the same carbon atom.

Experimental

The compounds were purified by repeated distillation under reduced pressure.

Refractive index at 20° ± 0·05° was determined by means of an Abbé refractometer, model G (Zeiss), standarised for the sodium *D* line.

Density was determined in a pycnometer at 20°.

Infrared absorption spectra were determined in a double-beam spectrophotometer (Hilger model H-800) with optics of rock salt and automatic recording. The substances were used in liquid form (liquids or supercooled liquids) in capillary thickness. The wavelengths were controlled by means of a polystyrene film. The maximum experimental error was 3 cm.$^{-1}$.

1-*Chloro*-3-*nitropropan*-2-*ol* (X).—Chloroacetaldehyde (23·6 g., 0·3 mol.), in the form of an 80% aqueous solution of its hydrate (33 g.), was mixed with nitromethane (23 g., 0·38 mol.). Potassium carbonate (0·7 g.) in water (7 ml.) was added dropwise. The whole was warmed for 15 min. at 80°, then cooled to 35°. Dioxan (17 ml.) was added and whole left for 48 hr., then shaken with water and extracted with ether. The ether extract was shaken with a small quantity of concentrated hydrochloric acid, washed with water, dried, ($MgSO_4$), and evaporated. Two distillations under reduced pressure gave the *product*, b. p. 101—103°/6 mm. (5 g., 12%) (Found: N, 10·1. $C_3H_6ClNO_3$ requires N, 10·0%).

1,1,1,3-*Tetrachloro*-3-*nitropropan*-2-*ol* (XIII).—1,1,1-Trichloro-3-nitropropan-2-ol (XII) (83·2 g., 0·4 mole) was dissolved in methanol (40 ml.) and cooled to −5°. Sodium methoxide solution (from sodium, 9·2 g.; 0·4 g.-atom) (100 ml.) was added dropwise. The mixture was left at −10° for 24 hr. The precipitated sodium derivative of (XII) was collected and washed with ether (yield, 70·0 g., 76·5%).

This sodium derivative (35 g., 0·153 mole) was suspended in dry chloroform (65 ml.), and dry chlorine was introduced at −5°. Samples of the precipitate were taken from the reacting medium and ignited. The reaction was ended when the precipitate was composed of sodium chloride only. The chloroform solution was then filtered, washed with aqueous sodium hydrogen carbonate and water, and dried (Na_2SO_4). The solvent and the *product* (XIII) were distilled under reduced pressure. The fraction of b. p. 103—104°/0·7 mm. was collected (23·7 g., 64·0%) (Found: N, 6·0. $C_3H_3Cl_4NO_3$ requires N, 5·8%).

3-*Bromo*-1,1,1-*trichloro*-3-*nitropropan*-2-*ol* (XIV).—The sodium derivative (28 g., 0·122 mole) of the nitro-alcohol (XII) was suspended in anhydrous chloroform (60 ml.) and cooled to −5°. Bromine (17·5 g., 0·11 mole) in chloroform (10 ml.) was added dropwise until the mixture acquired a pale yellow colour. The sodium bromide was filtered off, and the solution washed with saturated aqueous sodium hydrogen carbonate and water. The solvent and the *product* (XIV) were distilled under reduced pressure. The fraction of b. p. 104—106°/0·8 mm. was collected (yield, 26·0 g., 74·4%) (Found: N, 4·85. $C_3H_2BrCl_3NO_3$ requires N, 4·9%).

1,1-*Dichloro*-3-*methyl*-3-*nitropropan*-2-*ol* (XVII).—Freshly distilled dichloroacetaldehyde (22·5 g., 0·2 mole) (prepared from dichloroacetal) was distilled with water (3·6 ml., 0·2 mole) and a drop of concentrated sulphuric acid, affording crystalline dichloroacetaldehyde hydrate (23 g., 0·175 mole), which was mixed with nitroethane (16·5 g., 0·22 mole) and warmed to 50° with stirring. Potassium hydrogen carbonate (0·4 g.) was added, the temperature rising spontaneously to 63°. After the reaction subsided the whole was warmed to 70° and left to cool with continuous mixing. The aqueous layer was collected and the organic layer washed three times with water. The combined aqueous solutions were extracted with ether, and the extract was washed several times with aqueous sodium hydrogen sulphite, then with saturated solution of sodium chloride, and dried ($MgSO_4$). Ether and the *product* (XVII) were distilled under reduced pressure. The fraction of b. p. 110—116°/2 mm. was collected and redistilled at 113°/2 mm. (yield, 9·3 g., 28·2%) (Found: N, 7·2. $C_4H_7Cl_2NO_3$ requires N, 7·45%).

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[*Received, July 13th,* 1960.]

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263. *Delocalization and Magnetic Properties of the Phosphonitrilic Halides.*

By D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock.

The magnetic anisotropy due to π-electron delocalization is calculated for systems of alternating $p\pi$- and $d\pi$-orbitals, and compared with that for $p\pi$–$p\pi$ systems. Calculations on the London model show a strong dependence upon the electro-negativity difference between the $p\pi$- and $d\pi$-orbitals, and for realistic values the contribution is small compared with that in benzene. If the $d\pi$-orbitals are d_{xz}, tangentially directed, the π-electron contribution is small and paramagnetic; if d_{yz}-orbitals participate also, their influence is opposite in sign, leading to a steadily diminishing paramagnetic behaviour until, with equal participation by d_{xz}- and d_{yz}-orbitals, the π-electron ring current contribution is close to zero

Measurement of diamagnetic anistropy are reported for $(PNCl_2)_3$, and of average susceptibility for $(PNCl_2)_n$, $n = 3$, 4, 5, 6, and 7. These measurements are compatible with a small paramagnetic or zero contribution by π-electrons but cannot be interpreted in detail to settle the degree of participation by d_{yz}-orbitals.

Energy calculations including d_{yz}-orbitals suggest that in the phosphonitrilic compounds these orbitals are used to some extent as well as the dominant d_{xz}-type.

We first report two sets of calculations on cyclic systems of alternating $p\pi$- and $d\pi$-orbitals, such as occur in the phosphonitrilic and thiazyl halides,[1,2] and in some other ring systems. The effect on the π-electron energetics of the inclusion of the second, radially directed $d\pi$-orbital (d_{yz} in the convention of ref. 2) is first considered, and then the contribution to the diamagnetic susceptibility made by π-electrons which are delocalized in $p\pi$–$d\pi$ systems is calculated and compared with that in $p\pi$–$p\pi$ systems.

The method for dealing with the energetics of delocalization involving both d_{xz}- and d_{yz}-types of $d\pi$-orbitals in a $p\pi$–$d\pi$ system was given some time ago.[3] The systems treated are planar cyclic molecules of 4, 6, and 8 ring atoms, providing alternately $p\pi$-orbitals and a pair of $d\pi$-orbitals. The methods are those of simple molecular-orbital theory, framed in terms of a single resonance parameter δ, defined as the resonance integral for the interaction of neighbour $p\pi$- and $d\pi$-orbitals *oriented for maximum overlap*.* It is easily shown that the resonance integrals for the atoms arranged in planar rings are $h_{xz}\delta$ and $h_{yz}\delta$, with the h's given by the cosines of the angles made by the internuclear axis with the tangential and radial directions respectively. The electronegativity of the tangential (d_{xz}) orbital is α; that of the $p\pi$-orbital, being more electronegative, is $\alpha + \rho\delta$, ρ being a parameter taking zero or positive values. The d_{yz}-orbital will have (i) electronegativity α, or (ii) $\alpha - \delta$, or (iii) for purposes of comparison it will be supposed not to take part at all, as in earlier calculations. Since the d_{xz}-orbital will be more strongly perturbed by neighbouring atoms than the d_{yz}, the only situations that are realistic are those in which d_{xz} is made the more electronegative atomic orbital. Thus cases (i) and (iii) are limiting cases, and (ii) is a representative intermediate case.

The general secular equation for orbital energies may be written as follows, with the substitution $x = (\alpha - E)/\delta$, and with an unspecified electronegativity parameter α_{yz} for the d_{yz}-orbital:

$$\begin{vmatrix} x+\rho & 2i\sin(l\pi/n)\,h_{xz} & 2\cos(l\pi/n)\,h_{yz} \\ -2i\sin(l\pi/n)\,h_{xz} & x & 0 \\ 2\cos(l\pi/n)\,h_{yz} & 0 & (\alpha_{yz}-E)/\delta \end{vmatrix} = 0 \quad . \quad . \quad . \quad (1)$$

* This change from the definition of refs. 1, 2, and 3, helps the formulation of the two $d\pi$-orbital problem.

[1] Craig and Paddock, *Nature*, 1958, **181**, 1052.
[2] Craig, *J.*, 1959, 997.
[3] Craig, *Chem. Soc. Spec. Publ.* No. 12, 1958, p. 343.

in which l is the ring quantum number and $2n$ is the number of atoms in the ring. By solving this equation, summing the energies of the occupied orbitals, and subtracting the energy of a " structure " consisting of n two-electron bonds made up from the $p\pi$-orbital on the nitrogen atoms and the pair of appropriately directed $d\pi$-orbitals on the phosphorus atoms we get the delocalization energy. This quantity, divided by the number of π-electrons in the system, is listed in Table 1 for several cases.

TABLE 1. *Delocalization energy per π-electron in $p\pi$–$d\pi$ systems.** (*In units of the resonance parameter δ*).

	$\rho = 0$	$\rho = 0{\cdot}5$	$\rho = 1{\cdot}0$	$\rho = 2{\cdot}0$
$n = 2$	0·41	0·41	0·38	0·32
	0·35	0·36	0·34	0·29
	0	0·07	0·12	0·14
$n = 3$	0·39	0·38	0·36	0·30
	0·30	0·32	0·32	0·30
	0·13	0·19	0·22	0·22
$n = 4$	0·43	0·42	0·40	0·34
	0·29	0·30	0·31	0·28
	0·19	0·23	0·25	0·24

* The first value in each block is calculated for equal electronegativities of d_{xz} and d_{yz}, the second for d_{yz} less electronegative by δ, and the third for participation by d_{xz} alone.

The gain in delocalization energy due to inclusion of the d_{yz}-orbital is relatively greater in the systems of 4 π-electrons than in those of 6 and 8. Thus, if in the real molecules

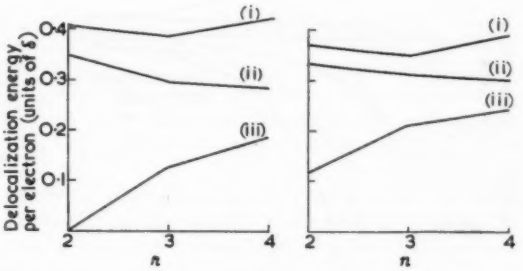

FIG. 1. *Delocalization energies for various $(AB)_n$ $p\pi$–$d\pi$ systems.*

(i) *Including d_{xz} and d_{yz} orbitals with equal electronegativity α.* (ii) *Including d_{xz} and d_{yz} orbitals, with d_{yz} less electronegative by δ.* (iii) *d_{xz} Orbital alone.*

Left-hand diagram: $\rho = 0$
Right-hand diagram: $\rho = 1$

the electronegativities of the d-orbitals permit substantial participation by both types, the 4- and 8-electron systems could be more stabilized than the 6-electron system. This might be described as *anti*-Hückel behaviour, since it is contrary to the Hückel rule which, in the $p\pi$–$p\pi$ aromatic series, associates aromatic behaviour with 6, 10, 14 . . . electron systems, and not with 4, 8, 12 . . . systems. The delocalization energies per π-electron for the cases $\rho = 0$ and 1 are given in Fig. 1. It is necessary to emphasise that these results are in terms of a common unit δ; and it is an approximation to neglect variations of δ with ρ and to assume, in the second entry in each block of Table 1, that the same δ applies to the two different $p\pi$–$d\pi$ resonance integrals. Moreover, the total population of the d-orbitals is greater the more available the d_{yz}-orbital is assumed to be: this increase in population should perhaps be reflected in a promotion energy term. That is, the total energy of the system may be higher when both d-orbitals are included on account of increased intra-atomic electron repulsion. This would reduce the energetic advantage shown in Table 1 for the first two entries in each block. In spite of these points, however, it seems clear that use of the d_{yz}-orbitals results in some energy gain, and therefore that they will be used to some extent in the delocalized system.

Although the qualitative features of the energy calculations are not much changed by the inclusion of the d_{yz}-orbital, there is a considerable influence on the contribution made by the delocalized electrons to the diamagnetic susceptibility. It was shown many years

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of same length and structure of carbon chain: for these, as we shall detail elsewhere,[8] the frequencies symmetric NO_2 vibrations are the same within experimental error (~3 cm.$^{-1}$). For instance, the spectrum of 1-chloro-1-nitropropane-2-ol (VIII) has strong bands at 1384 and 1367 cm.$^{-1}$; the spectrum of 1-chloro-1-nitropropane has a strong band 1364 cm.$^{-1}$, indicating the second of the above values as corresponding to symmetric NO_2 vibrations.

TABLE 2. *Some frequencies in the infrared absorption spectra.*

No.	Band frequencies (cm.$^{-1}$)
I	3551—3415m(b), 1554vs, 1421m, 1375s
II	3552—3405m(b), 3011m, 1571vs, 1353s
III	3539—3390m(b), 3023w, 1566vs, 1353m
IV	3533—3406s(b), 1584vs, 1325s, 899s, 847s
V	3532—3397m(b), 1579vs, 1324s
VI	3554—3430m(b), 1569vs, 1323s
VII	3538—3418s(b), 1552vs, 1423s, 1386s
VIII	3541—3427s(b), 1570vs, 1384s, 1367s, 1335w
IX	3535—3425m(b), 1566vs, 1365s
X	3537—3440m(b), 3026vw, 1553vs, 1423m, 1384s
XI	3534m(b), 3006vw, 1555vs, 1418m, 1379s, 790s
XII *	3525s(b), 3028w, 1558vs, 1419s, 1377s, 807vs
XIII	3518s(b), 3006w, 1579vs, 1355s, 822s, 803s
XIV	3509m(b), 3006w, 1566vs, 1353s, 825s
XV	3539—3452m(b), 1545vs, 1389s, 1361m
XVI	3531—3433m(b), 3004m, 1549vs, 1391m, 1362m
XVII	3526s(b), 3003m, 1549vs, 1391s, 1362s, 783s
XVIII	3526m(b), 3004vw, 1549vs, 1390m, 1357s, 824s, 797s
XIX	3543—3428s(b), 1553vs, 1421s, 1385s
XX	3538—3443s(b), 1572vs, 1368s, 1350s, 1331s
XXI	3545—3453s(b), 1565vs, 1366s
XXII	3549—3444s(b), 1553vs, 1424s, 1385s
XXIII	3530—3414m(b), 1570vs, 1370m, 1355m
XXIV *	3541—3447m(b), 1563vs, 1356s
XXV	3529m(b), 3039vw, 1556vs, 1417m, 1382s, 812s
XXVI	3535—3456m(b), 1551vs, 1418m, 1381s
XXVII	3538—3436s(b), 1552vs, 1422s, 1385s
XXVIII	3544—3442m(b), 1566vs, 1368s, 1353s
XXIX	3534—3435m(b), 1557vs, 1353s
XXX	3541—3449m(b), 1550vs, 1417m, 1381s
XXXI	3524—3448m(b), 1545vs, 1422sh, 1382s
XXXII	3538—3483m(b), 1562vs, 1353s
XXXIII	3537—3449m(b), 1556vs, 1350s
XXXIV	3541—3454m(b), 1550vs, 1417m, 1381s
XXXV	3522—3416m(b), 1550vs, 1419m, 1384s
XXXVI	3545—3476m(b), 1571vs, 1366m
XXXVII	3551—3457m(b), 1566vs, 1356m
XXXVIII	3534—3443m(b), 1551vs, 1416m, 1378s
XXXIX	3537—3438m(b), 1551vs, 1417m, 1377s
XL	3541—3451m(b), 1550vs, 1418m, 1379s

* Measurements of supercooled liquid.

We could not confirm the frequency 1340 cm.$^{-1}$ assigned by Haszeldine[1] for 1-chloro-1-nitropropane as we found only a weak band 1335 cm.$^{-1}$ in this compound which could not be assigned to the frequency in question. Similarly, 1-chloro-1-nitropentan-2-ol (XXIII) has bands at 1370 and 1355 cm.$^{-1}$, and the second was chosen as it is identical with the frequency of symmetric NO_2 vibrations of 1-chloro-1-nitropentane (1355 cm.$^{-1}$).

Comparison of the spectrum of a nitro-alcohol with that of the corresponding nitroparaffin does not always give a simple solution. 1-Chloro-1-nitrobutan-2-ol (XX) gives bands of almost identical intensity (strong) at 1368, 1350, and 1331 cm.$^{-1}$. The 1-chloro-1-nitrobutane gives a strong band at 1355 with a shoulder 1367 cm.$^{-1}$. Eventually we assigned the band 1368 cm.$^{-1}$ to symmetric NO_2 vibrations.

Broadly speaking, no general method of identification of bands of symmetric NO_2 vibrations exists, and the assignment is not always certain. The assignments made are

[8] Urbański, Eckstein, Sobótka, and Gluziński, unpublished work.

recorded in Table 3. The shift due to chlorine and bromine atom in the position 1 is in the direction of lower frequency, *i.e.*, in the opposite direction to that for asymmetric vibrations. The lowering is relatively strong and amounts to 17—32 cm.$^{-1}$. No difference between the action of chlorine and bromine was noticed, except for the derivatives of cyclohexylnitroethanol (XXXVI and XXXVII respectively) where the bromo-compound had a frequency lower by 10 cm.$^{-1}$.

TABLE 3. *Comparison of frequencies of the nitro-group in nitro-alcohols and their halogen* (Cl *and* Br) *derivatives.*

No.	Compound *	$\nu(NO_2)$ (cm.$^{-1}$) asymm.	symm.	No.	Compound *	$\nu(NO_2)$ (cm.$^{-1}$) asymm.	symm.
I	$HO{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2$	1554	1375	II	$HO{\cdot}CH_2{\cdot}CHCl{\cdot}NO_2$	1571	1353
				III	$HO{\cdot}CH_2{\cdot}CHBr{\cdot}NO_2$	1566	1353
				IV	$HO{\cdot}CH_2{\cdot}CCl_2{\cdot}NO_2$	1584	1325
				V	$HO{\cdot}CH_2{\cdot}CBrCl{\cdot}NO_2$	1579	1324
				VI	$HO{\cdot}CH_2{\cdot}CBr_2{\cdot}NO_2$	1569	1323
VII	$CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1552	1386	VIII	$CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1570	1367
				IX	$CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1566	1365
				X	$CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1553	1384
				XI	$CHCl_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1555	1379
				XII †	$CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1558	1377
				XIII	$CCl_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1579	1355
				XIV	$CCl_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1566	1358
XV	$CH_2{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1545	1361	XVI	$CH_2Cl{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1549	1364
				XVII	$CHCl_2{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1549	1362
				XVIII	$CCl_2{\cdot}CH(OH){\cdot}CHMe{\cdot}NO_2$	1549	1357
XIX	$CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1553	1385	XX	$CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1572	1368
				XXI	$CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1565	1366
XXII	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1553	1385	XXIII	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1570	1355
				XXIV †	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1563	1356
				XXV	$CH_2{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1556	1382
XXVII	$Me_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1552	1385	XXVIII	$Me_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1566	1353
				XXIX	$Me_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1557	1353
XXXI	$C_6H_{10}(OH){\cdot}CH_2{\cdot}NO_2$	1545	1382	XXXII	$C_6H_{10}(OH){\cdot}CHCl{\cdot}NO_2$	1562	1353
				XXXIII	$C_6H_{10}(OH){\cdot}CHBr{\cdot}NO_2$	1556	1350
XXXV	$C_6H_{11}{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$	1550	1384	XXXVI	$C_6H_{11}{\cdot}CH(OH){\cdot}CHCl{\cdot}NO_2$	1571	1366
				XXXVII	$C_6H_{11}{\cdot}CH(OH){\cdot}CHBr{\cdot}NO_2$	1566	1356

* C_6H_{10} denotes cyclohexylidene. † Measurements of a supercooled liquid.

Two halogen atoms (IV—VI) produce a greater shift (50—52 cm.$^{-1}$), the same for chlorine as for bromine.

When chlorine atoms were introduced at position 3 only an insignificant shifting of symmetric vibrations (−3 to −9 cm.$^{-1}$) was observed. Replacement at position 1 and 3 (XIII, XIV) had a considerably greater effect.

The observed shifts of the bands of the nitro-group are in agreement with the findings by Haszeldine [1] and Brown [2] for the chlorine and bromine derivatives of nitroparaffins.

It seems to us that the shifts of the NO_2 frequencies can be explained (at least partly) by the fact that replacement at position 1 changes the nature of the nitro-compound. It is known that both bands of NO_2 vibrations for aliphatic secondary nitro-compounds are at lower frequencies than are those of aliphatic primary nitro-compounds. One halogen atom at position 1 produces a secondary nitro-compound and the final result is composed of two superposed partial effects, (1) that of the halogen, and (2) that of the nature of the nitro-group. For asymmetric NO_2 vibrations the effect (1) produces a shift to higher and effect (2) to lower frequencies; a higher frequency results which denotes the greater power of effect (1). For symmetric NO_2 vibrations both effects are in the same direction and a relatively large lowering of the frequency results.

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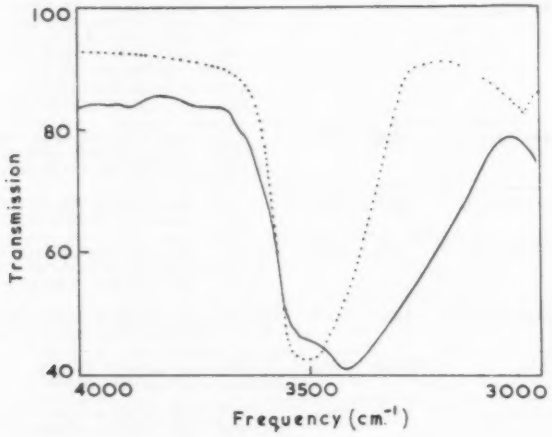
Hydroxyl Group.—All our nitro-alcohols give an absorption band between 3554 and 3390 cm.$^{-1}$ characterising the O–H stretching vibration. This band is broad and of middle intensity, indicating intermolecular hydrogen bonds. Two maxima (3554—3509 and 3483—3390 cm.$^{-1}$; full line in Figure) are observed. When two or three atoms of chlorine are attached at position 3 the second maximum disappears and the band becomes narrower (dotted line): this may signify that one type of hydrogen bond disappears for these compounds.

It should also be pointed out that the acidity of the hydroxyl groups is greater for the 3-trichloro-derivatives. This can be deduced by analogy with trichloroethanol: it may have a bearing on the ability to form hydrogen bonds.

Band at 3039—3003 *cm.*$^{-1}$.—A weak band at 3039—3003 cm.$^{-1}$ was noticed for all the halogenonitro-alcohols containing one or more halogen atoms at position 3. This band is

O–H *stretching vibrations of* 1-*nitropropan*-2-*ol* (*full line*) *and* 1,1-*dichloro*-3-*nitropropan*-2-*ol* (*dotted line*).



not present for unsubstituted nitro-alcohols and present only for some substituted products, such as 2-chloro- and 2-bromo-2-nitroethanol (II and III). Plyler and Benedict [9] found a similar band in the spectra of alkyl chlorides. It may be due to some C–H vibrations.

Band at 1424—1416 *cm.*$^{-1}$.—This band was found in all our nitro-alcohols containing primary nitro-groups. It is of high or medium intensity. Similar bands were reported by Brown.[2] They are probably produced by the scissors vibrations of the C–H bonds in the $CH_2{\cdot}NO_2$ group. Urbański [10] reported bands of frequencies 4167 and 3704 cm.$^{-1}$ for similar nitro-alcohols and these are probably overtones of the band in question.

Band at 1391—1389 *cm.*$^{-1}$.—A strong band of this frequency was found in the spectra of all the nitro-alcohols with a system $CH_3{\cdot}C{\cdot}NO_2$ (XV—XVIII), also by Brown,[2] according to whom it is due to deformation vibrations of C–H bonds in the methyl group attached to $C{\cdot}NO_2$.

Bands at 825—783 *cm.*$^{-1}$.—Strong and very strong bands 825—783 cm.$^{-1}$ are present in the spectra of all the nitro-alcohols containing two and three chlorine atoms at position 3 (XII—XIV, XVII—XVIII, XXV). They are probably formed by the vibrations of the groups CCl_2 and CCl_3. However the literature [11] reports lower frequencies (780—710 cm.$^{-1}$).

[9] Plyler and Benedict, *J. Res. Nat. Bur. Standards*, 1951, **47**, 202.
[10] Urbański, *Bull. Acad. Polon. Sci., Cl. III*, 1956, **4**, 87; 1956, **4**, 381; *Roczniki Chem.*, 1957, **31**, 37.
[11] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

Also strong bands at 899 and 847 cm.$^{-1}$ in the spectrum of 2,2-dichloro-2-nitroethanol (IV) may be assigned to CCl_2 and their shift to higher frequency may be due to the presence of the NO_2 group attached to the same carbon atom.

Experimental

The compounds were purified by repeated distillation under reduced pressure.

Refractive index at 20° ± 0·05° was determined by means of an Abbé refractometer, model G (Zeiss), standarised for the sodium *D* line.

Density was determined in a pycnometer at 20°.

Infrared absorption spectra were determined in a double-beam spectrophotometer (Hilger model H-800) with optics of rock salt and automatic recording. The substances were used in liquid form (liquids or supercooled liquids) in capillary thickness. The wavelengths were controlled by means of a polystyrene film. The maximum experimental error was 3 cm.$^{-1}$.

1-*Chloro*-3-*nitropropan*-2-*ol* (X).—Chloroacetaldehyde (23·6 g., 0·3 mol.), in the form of an 80% aqueous solution of its hydrate (33 g.), was mixed with nitromethane (23 g., 0·38 mol.). Potassium carbonate (0·7 g.) in water (7 ml.) was added dropwise. The whole was warmed for 15 min. at 80°, then cooled to 35°. Dioxan (17 ml.) was added and whole left for 48 hr., then shaken with water and extracted with ether. The ether extract was shaken with a small quantity of concentrated hydrochloric acid, washed with water, dried, ($MgSO_4$), and evaporated. Two distillations under reduced pressure gave the *product*, b. p. 101—103°/6 mm. (5 g., 12%) (Found: N, 10·1. $C_3H_6ClNO_3$ requires N, 10·0%).

1,1,1,3-*Tetrachloro*-3-*nitropropan*-2-*ol* (XIII).—1,1,1-Trichloro-3-nitropropan-2-ol (XII) (83·2 g., 0·4 mole) was dissolved in methanol (40 ml.) and cooled to −5°. Sodium methoxide solution (from sodium, 9·2 g.; 0·4 g.-atom) (100 ml.) was added dropwise. The mixture was left at −10° for 24 hr. The precipitated sodium derivative of (XII) was collected and washed with ether (yield, 70·0 g., 76·5%).

This sodium derivative (35 g., 0·153 mole) was suspended in dry chloroform (65 ml.), and dry chlorine was introduced at −5°. Samples of the precipitate were taken from the reacting medium and ignited. The reaction was ended when the precipitate was composed of sodium chloride only. The chloroform solution was then filtered, washed with aqueous sodium hydrogen carbonate and water, and dried (Na_2SO_4). The solvent and the *product* (XIII) were distilled under reduced pressure. The fraction of b. p. 103—104°/0·7 mm. was collected (23·7 g., 64·0%) (Found: N, 6·0. $C_3H_3Cl_4NO_3$ requires N, 5·8%).

3-*Bromo*-1,1,1-*trichloro*-3-*nitropropan*-2-*ol* (XIV).—The sodium derivative (28 g., 0·122 mole) of the nitro-alcohol (XII) was suspended in anhydrous chloroform (60 ml.) and cooled to −5°. Bromine (17·5 g., 0·11 mole) in chloroform (10 ml.) was added dropwise until the mixture acquired a pale yellow colour. The sodium bromide was filtered off, and the solution washed with saturated aqueous sodium hydrogen carbonate and water. The solvent and the *product* (XIV) were distilled under reduced pressure. The fraction of b. p. 104—106°/0·8 mm. was collected (yield, 26·0 g., 74·4%) (Found: N, 4·85. $C_3H_2BrCl_3NO_3$ requires N, 4·9%).

1,1-*Dichloro*-3-*methyl*-3-*nitropropan*-2-*ol* (XVII).—Freshly distilled dichloroacetaldehyde (22·5 g., 0·2 mole) (prepared from dichloroacetal) was distilled with water (3·6 ml., 0·2 mole) and a drop of concentrated sulphuric acid, affording crystalline dichloroacetaldehyde hydrate (23 g., 0·175 mole), which was mixed with nitroethane (16·5 g., 0·22 mole) and warmed to 50° with stirring. Potassium hydrogen carbonate (0·4 g.) was added, the temperature rising spontaneously to 63°. After the reaction subsided the whole was warmed to 70° and left to cool with continuous mixing. The aqueous layer was collected and the organic layer washed three times with water. The combined aqueous solutions were extracted with ether, and the extract was washed several times with aqueous sodium hydrogen sulphite, then with saturated solution of sodium chloride, and dried ($MgSO_4$). Ether and the *product* (XVII) were distilled under reduced pressure. The fraction of b. p. 110—116°/2 mm. was collected and redistilled at 113°/2 mm. (yield, 9·3 g., 28·2%) (Found: N, 7·2. $C_4H_7Cl_2NO_3$ requires N, 7·45%).

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[*Received, July 13th,* 1960.]

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263. *Delocalization and Magnetic Properties of the Phosphonitrilic Halides.*

By D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock.

The magnetic anisotropy due to π-electron delocalization is calculated for systems of alternating $p\pi$- and $d\pi$-orbitals, and compared with that for $p\pi$–$p\pi$ systems. Calculations on the London model show a strong dependence upon the electro-negativity difference between the $p\pi$- and $d\pi$-orbitals, and for realistic values the contribution is small compared with that in benzene. If the $d\pi$-orbitals are d_{xz}, tangentially directed, the π-electron contribution is small and paramagnetic; if d_{yz}-orbitals participate also, their influence is opposite in sign, leading to a steadily diminishing paramagnetic behaviour until, with equal participation by d_{xz}- and d_{yz}-orbitals, the π-electron ring current contribution is close to zero

Measurement of diamagnetic anistropy are reported for $(PNCl_2)_3$, and of average susceptibility for $(PNCl_2)_n$, $n = 3$, 4, 5, 6, and 7. These measurements are compatible with a small paramagnetic or zero contribution by π-electrons but cannot be interpreted in detail to settle the degree of participation by d_{yz}-orbitals.

Energy calculations including d_{yz}-orbitals suggest that in the phosphonitrilic compounds these orbitals are used to some extent as well as the dominant d_{xz}-type.

We first report two sets of calculations on cyclic systems of alternating $p\pi$- and $d\pi$-orbitals, such as occur in the phosphonitrilic and thiazyl halides,[1,2] and in some other ring systems. The effect on the π-electron energetics of the inclusion of the second, radially directed $d\pi$-orbital (d_{yz} in the convention of ref. 2) is first considered, and then the contribution to the diamagnetic susceptibility made by π-electrons which are delocalized in $p\pi$–$d\pi$ systems is calculated and compared with that in $p\pi$–$p\pi$ systems.

The method for dealing with the energetics of delocalization involving both d_{xz}- and d_{yz}-types of $d\pi$-orbitals in a $p\pi$–$d\pi$ system was given some time ago.[3] The systems treated are planar cyclic molecules of 4, 6, and 8 ring atoms, providing alternately $p\pi$-orbitals and a pair of $d\pi$-orbitals. The methods are those of simple molecular-orbital theory, framed in terms of a single resonance parameter δ, defined as the resonance integral for the interaction of neighbour $p\pi$- and $d\pi$-orbitals *oriented for maximum overlap*.* It is easily shown that the resonance integrals for the atoms arranged in planar rings are $h_{xz}\delta$ and $h_{yz}\delta$, with the h's given by the cosines of the angles made by the internuclear axis with the tangential and radial directions respectively. The electronegativity of the tangential (d_{xz}) orbital is α; that of the $p\pi$-orbital, being more electronegative, is $\alpha + \rho\delta$, ρ being a parameter taking zero or positive values. The d_{yz}-orbital will have (i) electronegativity α, or (ii) $\alpha - \delta$, or (iii) for purposes of comparison it will be supposed not to take part at all, as in earlier calculations. Since the d_{xz}-orbital will be more strongly perturbed by neighbouring atoms than the d_{yz}, the only situations that are realistic are those in which d_{xz} is made the more electronegative atomic orbital. Thus cases (i) and (iii) are limiting cases, and (ii) is a representative intermediate case.

The general secular equation for orbital energies may be written as follows, with the substitution $x = (\alpha - E)/\delta$, and with an unspecified electronegativity parameter α_{yz} for the d_{yz}-orbital:

$$\begin{vmatrix} x+\rho & 2i\sin(l\pi/n)\,h_{xz} & 2\cos(l\pi/n)\,h_{yz} \\ -2i\sin(l\pi/n)\,h_{xz} & x & 0 \\ 2\cos(l\pi/n)\,h_{yz} & 0 & (\alpha_{yz}-E)/\delta \end{vmatrix} = 0 \quad . \quad . \quad . \quad (1)$$

* This change from the definition of refs. 1, 2, and 3, helps the formulation of the two $d\pi$-orbital problem.

[1] Craig and Paddock, *Nature*, 1958, **181**, 1052.
[2] Craig, *J.*, 1959, 997.
[3] Craig, *Chem. Soc. Spec. Publ.* No. 12, 1958, p. 343.

in which l is the ring quantum number and $2n$ is the number of atoms in the ring. By solving this equation, summing the energies of the occupied orbitals, and subtracting the energy of a " structure " consisting of n two-electron bonds made up from the $p\pi$-orbital on the nitrogen atoms and the pair of appropriately directed $d\pi$-orbitals on the phosphorus atoms we get the delocalization energy. This quantity, divided by the number of π-electrons in the system, is listed in Table 1 for several cases.

TABLE 1. *Delocalization energy per π-electron in* pπ–dπ *systems.** (*In units of the resonance parameter* δ).

	$\rho = 0$	$\rho = 0{\cdot}5$	$\rho = 1{\cdot}0$	$\rho = 2{\cdot}0$
$n = 2$	0·41	0·41	0·38	0·32
	0·35	0·36	0·34	0·29
	0	0·07	0·12	0·14
$n = 3$	0·39	0·38	0·36	0·30
	0·30	0·32	0·32	0·30
	0·13	0·19	0·22	0·22
$n = 4$	0·43	0·42	0·40	0·34
	0·29	0·30	0·31	0·28
	0·19	0·23	0·25	0·24

* The first value in each block is calculated for equal electronegativities of d_{xz} and d_{yz}, the second for d_{y^2} less electronegative by δ, and the third for participation by d_{xz} alone.

The gain in delocalization energy due to inclusion of the d_{yz}-orbital is relatively greater in the systems of 4 π-electrons than in those of 6 and 8. Thus, if in the real molecules

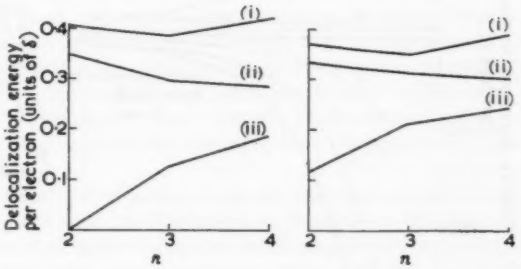

FIG. 1. *Delocalization energies for various* $(AB)_n$ *pπ–dπ systems.*

(i) *Including d_{xz} and d_{yz} orbitals with equal electronegativity* α. (ii) *Including d_{xz} and d_{yz} orbitals, with d_{yz} less electronegative by* δ. (iii) *d_{xz} Orbital alone.*

Left-hand diagram: $\rho = 0$
Right-hand diagram: $\rho = 1$

the electronegativities of the d-orbitals permit substantial participation by both types, the 4- and 8-electron systems could be more stabilized than the 6-electron system. This might be described as *anti*-Hückel behaviour, since it is contrary to the Hückel rule which, in the $p\pi$–$p\pi$ aromatic series, associates aromatic behaviour with 6, 10, 14 . . . electron systems, and not with 4, 8, 12 . . . systems. The delocalization energies per π-electron for the cases $\rho = 0$ and 1 are given in Fig. 1. It is necessary to emphasise that these results are in terms of a common unit δ; and it is an approximation to neglect variations of δ with ρ and to assume, in the second entry in each block of Table 1, that the same δ applies to the two different $p\pi$–$d\pi$ resonance integrals. Moreover, the total population of the d-orbitals is greater the more available the d_{yz}-orbital is assumed to be: this increase in population should perhaps be reflected in a promotion energy term. That is, the total energy of the system may be higher when both d-orbitals are included on account of increased intra-atomic electron repulsion. This would reduce the energetic advantage shown in Table 1 for the first two entries in each block. In spite of these points, however, it seems clear that use of the d_{yz}-orbitals results in some energy gain, and therefore that they will be used to some extent in the delocalized system.

Although the qualitative features of the energy calculations are not much changed by the inclusion of the d_{yz}-orbital, there is a considerable influence on the contribution made by the delocalized electrons to the diamagnetic susceptibility. It was shown many years

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ago by London [4] that the exaltation of diamagnetism measured perpendicular to the ring plane in normal aromatic molecules may be accounted for by considering the induction of peripheral electron currents in the π-electron system. London's methods may be applied to deal with alternating $(AB)_n$ $p\pi$–$p\pi$ systems and $p\pi$–$d\pi$ systems. The first permit the calculation of the changed diamagnetism of molecules such as 1,3,5-triazine and borazole in which electronegativity differences occur in the ring atoms. The results in this case are in no way surprising (Fig. 2, upper half). They show that in $p\pi$–$p\pi$ delocalization the diamagnetism due to the induced ring current dies away as the electronegativity difference increases, *i.e.*, it decreases as the delocalization decreases. The dependence of the orbital energies on the magnetic field $\boldsymbol{H}$ is expressed in the secular equation (2):

$$\begin{vmatrix} x+\rho & 2\cos(l\pi/n+\theta) \\ 2\cos(l\pi/n+\theta) & x \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The two species of ring atom have electronegativities differing by ρ units of the appropriate resonance integral, and the field dependence is contained in the angle θ, $\theta = 2\pi\boldsymbol{H}\beta S/2n$, where S is the (signed) area of the ring, and $\beta = e/hc$.[5] The cosine form of the off-diagonal elements ensures that the binding energies of the occupied orbitals will be reduced or

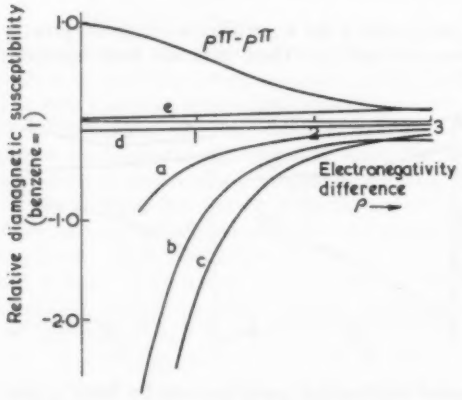

FIG. 2. *Contributions to the magnetic susceptibility normal to the ring plane for* $(AB)_n$ *ring systems.* ρ *is the electronegativity difference between the participating orbitals in units of the resonance integral. The susceptibility unit is the calculated value for benzene,* δ *being assumed constant.*

Top curve: normal six-membered $p\pi$–$p\pi$ *aromatic series.*

(a) d_{xz}- *and* $p\pi$-*orbitals only, in a 4-ring.* (b) d_{xz} *and* $p\pi$, *6-ring.* (c) d_{xz} *and* $p\pi$, *8-ring.* (d) d_{xz}, d_{yz}, *and* $p\pi$, *6-ring.* (e) d_{xz}, d_{yz}, *and* $p\pi$, *8-ring.*

left unchanged in the presence of a field, leading to diamagnetic behaviour. Also, as ρ increases, corresponding to an increased electronegativity increase between the ring atoms, the influence of the off-diagonal terms is less, allowing the diamagnetism to fall away as shown in Fig. 2.

For $p\pi$–$d\pi$ systems we first consider the magnetic properties of a set of $p\pi$- and d_{xz}-orbitals only, as in case (iii) heretofore. The secular equation for the energies in a magnetic field, in the units as before, is:

$$\begin{vmatrix} x+\rho & 2i\sin(l\pi/n+\theta) \\ -2i\sin(l\pi/n+\theta) & x \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad (3)$$

For occupied orbitals with $l \neq 0$ the effect of the field is, again, to reduce the binding energy, giving a diamagnetic contribution, but a special situation occurs for the orbitals $l = 0$. In the absence of the field these two orbitals have different symmetries [2] and do not interact: the more stable (occupied) orbital consists solely of the more electronegative of the atomic orbitals, namely $p\pi$, and the less stable consists only of the less electronegative,

[4] London, *J. Phys. Radium*, 1957, **8**, 397.
[5] McWeeny, *Proc. Phys. Soc.*, 1951, **64**, *A*, 921.

namely d_{xz}. However, the magnetic field causes these molecular orbitals to interact with one another with the result that the lower, occupied, one is increased in binding energy. Electrons in this orbital behave paramagnetically, and their contribution outweighs the diamagnetism of the other electrons in the occupied orbitals, giving an overall paramagnetic contribution perpendicularly to the ring plane. This behaviour is illustrated in the lower half of Fig. 2. This effect gets less as the parameter ρ increases, as expected. As ρ drops toward zero the paramagnetism apparently increases without limit, but this is a false result because near $\rho = 0$ the single configuration approximation breaks down, and it would be essential to consider the orbital degeneracy problem as in the analogous example of cyclobutadiene.[6] Thus the magnetic instability of the $p\pi$-d_{xz} system suggested by Fig. 2 is not real. The considerations outlined for $p\pi$–d_{xz} systems hold word for word in $p\pi$–$p\pi$ systems of $4m$-electrons, *e.g.*, the plane regular octagonal model of cyclo-octatetraenes and its $(AB)_4$ analogues.

The inclusion of both d_{xz}- and d_{yz}-orbitals changes the expected magnetic behaviour completely. The secular equation including the field is found from (1) by replacing the angle $(\pi l/n)$ by $(\pi l/n + \theta)$; as usual, the diamagnetism is equal to the coefficient of $-(1/2)\boldsymbol{H}^2$ in the expression for the total energy as a function of $\boldsymbol{H}$. The examples given in Fig. 2 are for equally electronegative $d\pi$-orbitals: it is found that the π-electrons in these cases make a negligibly small contribution through delocalization. In the 4-membered ring the contribution is zero for all values of ρ. In the 6-membered ring it is feebly paramagnetic and in the 8-membered feebly diamagnetic. The contributions are all small compared with those from $p\pi$–$p\pi$ delocalization or for $p\pi$–d_{xz}.

It will be observed that the effect of d_{yz}-orbital participation in the delocalization is to add to the stabilization produced by $p\pi$–d_{xz} interaction, but to oppose the paramagnetic effect by a diamagnetic one which cancels it almost exactly. The magnetic results, applying as they do to case (i) of equally electronegative $d\pi$-orbitals, are for the extreme situation. The magnetism of examples with less electronegative d_{yz}-orbitals is more difficult to calculate, but from the form of the relationship it is clear that the results would be intermediate between the $p\pi$–d_{xz} case and the magnetically isotropic case of equally electronegative $d\pi$ orbitals.

Dewar *et al.*[7] have recently argued that the situation in $p\pi$–$d\pi$ systems is in fact that of equally electronegative d_{xz}- and d_{yz}-orbitals, as illustrated in the curves labelled (i) (Fig. 1) and (d) and (e) (Fig. 2). Dewar *et al.* show that the π-electron system then consists of "islands" or conjugated zones stretching over a nitrogen atom and two adjacent phosphorus atoms, with little conjugation between different islands. This leads them to conclude that the delocalization is not over the entire ring and therefore that the systems should not be described as aromatic. We think that this conclusion is not well founded, because it depends upon an exact, or nearly exact, equality of the electronegativities of the two $d\pi$-orbitals. If they are unequal, irrespective of which is the greater, the delocalization does involve the whole cyclic system to an extent which increases the more the two orbitals differ. Now there is nothing in the problem to support the idea of *exactly* equal $d\pi$-orbitals. The weakly bound d-orbitals of free phosphorus are easily polarizable by ligand atoms, and the degree of polarization of an orbital depends upon its directional properties in relation to the ligand environment. This is not symmetrical in relation to the two $d\pi$-orbitals, which must be differently affected by it. Dewar's procedure of simply taking for granted, in spite of this, that the orbitals are of equal electronegativity, and then drawing conclusions which depend critically on their equality, is open to question. We think that the relative electronegativities of d_{xz} and d_{yz} is an open question that will have to be settled by testing theory against experiment. Magnetic properties are interesting in this connection but, as will be shown, are not yet conclusive.

[6] Craig, *Proc. Roy. Soc.*, 1950, *A*, **202**, 498.
[7] Dewar, Lucken. and Whitehead, *J.*, 1960, 2423.

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Experimental

Results.—The results to be described are (i) the diamagnetic anistropy of single crystals of $(PNCl_2)_3$ and (ii) the average susceptibility of $(PNCl_2)_n$ for $n = 3$, 4, 5, 6, and 7.

The diamagnetic anistropy of single crystals of $(PNCl_2)_3$, determined by the critical torsion method,[8] is: $\chi_c - \chi_b = -8{\cdot}5 \times 10^{-6}$, $\chi_c - \chi_a = -6{\cdot}8 \times 10^{-6}$, and $\chi_a - \chi_b = -1{\cdot}7 \times 10^{-6}$ c.g.s. unit. Coupled with the mean susceptibility $\frac{1}{3}(\chi_a + \chi_b + \chi_c)$ of $-149{\cdot}3 \times 10^{-6}$ given by the Gouy method, these values lead to the following susceptibilities in the directions of crystal axes: $\chi_a = -147{\cdot}6 \times 10^{-6}$, $\chi_b = -145{\cdot}9 \times 10^{-6}$, and $\chi_c = -154{\cdot}4 \times 10^{-6}$ c.g.s. unit.

The molecular susceptibilities may be found from the crystal values by using the results of a recent *X*-ray analysis.[9] The molecules of $(PNCl_2)_3$ have a nearly planar skeleton of phosphorus and nitrogen atoms and a three-fold symmetry axis normal to the plane; the two in-plane susceptibilities K_1 and K_2 should therefore be equal. The value measured along a crystal axis is the sum of contributions by the principal molecular susceptibilities each multiplied by the square of the appropriate direction cosine.[10] By inverting this relationship we find the molecular susceptibilities: $K_1 = -145{\cdot}8 \times 10^{-6}$, $K_2 = -145{\cdot}9 \times 10^{-6}$, and $K_3 = -156{\cdot}3 \times 10^{-6}$ c.g.s. unit. The molecular diamagnetic anistropy of $(PNCl_2)_3$ is then:

$$\Delta K = K_3 - \tfrac{1}{2}(K_1 + K_2) = -10{\cdot}5 \times 10^{-6} \text{ c.g.s. unit}$$

Measurements by the Gouy method of the average susceptibilities of a series of cyclic polymers $(PNCl_2)_n$ are summarized in Table 2. The preparation and characterization of these compounds are described elsewhere.[11]

Table 2. *Average susceptibilities* $\bar{\chi}_M$ *for* $(PNCl_2)_n$.

Compound	$(PNCl_2)_3$	$(PNCl_2)_4$	$(PNCl_2)_5$	$(PNCl_2)_6$	$(PNCl_2)_7$
$\bar{\chi}_M$ ($\times 10^{-6}$ c.g.s.)	−149·3	−196·8	−248·1	−300·5	−342·5
Susceptibility per $PNCl_2$	−49·8	−49·2	−49·6	−50·1	−48·9

Discussion

The diamagnetic anistropy of benzene is -60×10^{-6} c.g.s. unit; that of $(PNCl_2)_3$ is $-10{\cdot}5 \times 10^{-6}$, and the analysis of this much smaller value requires an examination of the terms that can contribute to it. Hoarau [12] showed that in benzene only a part of the observed anistropy is due to ring currents. He discussed the anistropy of benzene and other aromatic hydrocarbons according to the scheme:

$$\Delta K = \Delta K_{\text{London}} + \Sigma \Delta k_\sigma + m \Delta k_\pi$$

The first term is the anisotropy according to the London theory, *i.e.*, the component due to ring currents in the delocalized π-electrons, and is the term of present interest. The second term represents the anisotropy due to σ-electrons, and the third arises from the π atomic orbitals,[13] and acts in the sense of reducing the in-plane components K_1 and K_2. It follows from Hoarau's analysis of the molecular susceptibilities in aromatic hydrocarbons that the ring current contribution is given to a good approximation by the expression:

$$\Delta K_{\text{London}} = K_3 - \Sigma \chi_A$$

We make the heuristic assumption, which cannot yet be adequately tested, that this formula applies generally, and use it in Table 4 to obtain ΔK_{London} for several molecules relevant to the discussion of $(PNCl_2)_3$. Table 3 lists the essential atomic susceptibility constants. The two benzene derivatives in Table 4 show large delocalization anisotropies,

[8] Krishnan and Banerjee, *Phil. Trans.*, 1934, **234**, 265.
[9] Wilson and Carroll, *J.*, 1960, 2548.
[10] Lonsdale and Krishnan, *Proc. Roy. Soc.*, 1936, *A*, **156**, 597.
[11] Lund, Paddock, Proctor, and Searle, *J.*, 1960, 2542.
[12] Hoarau, *Ann. Chim.* (*France*), 1956, **13**, 544.
[13] Berthier, Mayot, Pullman, and Pullman, *J. Phys. Radium*, 1952, **13**, 15.

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both somewhat reduced from benzene itself (-38×10^{-6}). Heterocyclic molecules, however, show very small values, reflecting the sensitivity to electronegativity differences apparent in the theoretical calculations illustrated in Fig. 2. These residual anisotropies are too small to be significant, as is shown by the negative result for cyanuric chloride.

TABLE 3. *Atomic susceptibility constants* ($-\chi_A \times 10^{-6}$ *c.g.s.*).

H	2·0	Cl	18·5
N	9·0	B	7·2 *
C	7·4	P	10·0 *

* Taken from "Selected Constants and Numerical Data, Diamagnetism and Paramagnetism," Masson, Paris, 1957, Vol. VII, p. 222.

TABLE 4. *Molecular susceptibilities* (*units*, -10^{-6} *c.g.s.*).

Compound	K_1	K_2	K_3	ΔK	$\frac{1}{2}(K_1 + K_2)$	$\Sigma\chi_A$	$K_3 - \Sigma\chi_A$
p-Dichlorobenzene [14]	75·8	63·8	117	47·2	69·8	89·4	27·6
Hexachlorobenzene [8]	128	128	182	54	128	155·4	26·6
2,4,6-Trichloro-1,3,5-triazine [15]	70·9	71·2	101·3	30·3	71	104·7	−3·4
1,3,5-Trichloroborazole [16]	97·6	97·3	115·3	17·9	97·4	110·1	5·2
$(PNCl_2)_3$	145·8	145·9	156·3	10·5	145·8	168	−11·7
Anthracene [17]	77·2	74·7	250·7	174·7	76	123·6	127·1
Phenazine [17]	55·9	54·7	222·4	167·1	55·3	122·8	99·6

The value $+11{\cdot}7 \times 10^{-6}$ for $(PNCl_2)_3$ is based upon $-10{\cdot}0 \times 10^{-6}$ for the atomic susceptibility of phosphorus. This value for the ring-current anisotropy, though uncertain in size, suggests that the π-electron contribution may in fact be of opposite sign to that in the benzene-like aromatic series, in agreement with theoretical expectation.

We must, however, consider further the atomic susceptibility of phosphorus upon which the result for $(PNCl_2)_3$ depends critically. It is possible to make use of the in-plane susceptibilities to get another estimate. For the molecules listed in Table 4 it is clear that $\frac{1}{2}(K_1 + K_2)$ is always less than $\Sigma\chi_A$ and especially so when sp^2-hybridized nitrogen is involved. Chlorine, however, makes its normal contribution in *p*-dichlorobenzene and in hexachlorobenzene, and will be assumed to do so also in $(PNCl_2)_3$. For the determination of the in-plane contribution by nitrogen we have the values for 2,4,6-trichloro-1,3,5-triazine and for phenazine. From the former we find that nitrogen contributes $-1{\cdot}2 \times 10^{-6}$ to the in-plane susceptibility, and from the latter $+1{\cdot}95 \times 10^{-6}$, instead of the average value of $-9{\cdot}0 \times 10^{-6}$ given in Table 3 and based on studies of saturated nitrogen compounds. The difference between the two determinations of the in-plane value is disturbing but not surprising, in view of the crudity of the procedure. By using these values in $(PNCl_2)_3$ we can get estimates of the in-plane contribution by phosphorus. The six chlorine atoms contribute -111×10^{-6} c.g.s. unit, and the three nitrogens either $-3{\cdot}6$ or $+5{\cdot}9 \times 10^{-6}$. In the first case the difference between the measured in-plane susceptibility of $-145{\cdot}8 \times 10^{-6}$ and the $-115{\cdot}8$ from the chlorine and nitrogen atoms is $-30{\cdot}0$, and in the second it is $-40{\cdot}7$, leading to values for phosphorus of $-10{\cdot}0$ and $-13{\cdot}6 \times 10^{-6}$ respectively. The anistropy of the atomic susceptibility being supposed small, as is likely in a nearly tetrahedrally hybridised atom, the calculated in-plane value should be close to the average χ_A. The first value of $-10{\cdot}0 \times 10^{-6}$ is, in fact, equal to the value given in Table 3 derived from non-cyclic saturated phosphorus compounds, and gives $+11{\cdot}7 \times 10^{-6}$ for the (paramagnetic) ring-current anisotropy term. The second leads to an even higher paramagnetic anistropy of $+22{\cdot}4 \times 10^{-6}$.

We consider finally the mean susceptibilities of the higher polymers, listed in Table 2. They show that the increment of susceptibility per $PNCl_2$ unit is closely constant. We

[14] Lemanceau, *J. Chim. phys.*, 1959, **56**, 933.
[15] Lonsdale, *Z. Krist.*, 1936, **95**, 471.
[16] Lonsdale and Toor, *Acta Cryst.*, 1959, **12**, 1048.
[17] Leela, Thesis, University of London, 1958.

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may deduce either that the ring-current contributions to $\bar{\chi}_M$ are small in all cases, or that the ring-current and the in-plane terms change in opposite, counteracting, senses as the size of the polymers increases. Although the latter seems unreasonable theoretically it cannot be ruled out by analysing experimental results now available. Our conclusion, which must therefore be tentative, is that both the diamagnetic anistropy of $(PNCl_2)_3$ and the mean susceptibilities of the several polymers are compatible with a ring-current contribution that is small, and probably paramagnetic, in all cases.

One of us (M. L. H.) acknowledges support by a CSIRO Postgraduate Studentship.

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[*Received, July 22nd,* 1960.]

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264. *The Nuclear Magnetic Resonance Spectra of Triphosphonitrilic 1,1-Difluoride 3,3,5,5-Tetrachloride.*

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The phosphorus and fluorine nuclear magnetic resonance spectra of triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride have been analysed as an AB_2X_2 system, by the full secular determinant method of Pople, Schneider, and Bernstein. The fluorine spectrum was obtained at two field strengths to provide a check on the assignments and to confirm the relative signs of the three spin-coupling constants. The appearance of positive and negative coupling constants in this molecule may have some bearing on the assumed $d\pi$–$p\pi$-aromatic delocalisation in the phosphonitrilic halide systems.

IT has recently been shown [1] that the compound $P_3N_3Cl_4F_2$ is triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride. In nuclear magnetic resonance spectroscopy this compound provides an example of an AB_2X_2 spin system in which there are three different spin-coupling constants J_{AX}, J_{BX}, and J_{AB} (defined as shown in Fig. 1) together with a

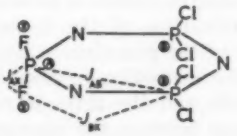

FIG. 1. *Spin-coupling constants in the* AB_2X_2 *system* $P_3N_3Cl_4F_2$.

field-dependent phosphorus chemical shift. The expected transition energies and relative intensities for this system may be obtained explicitly by an analysis similar to that used for simpler cases by Pople, Schneider, and Bernstein.[2]

The 32 basic symmetry functions for this system may be written down in such a way that they are products of the symmetry functions for the sets AB_2 and X_2. Because two of the interacting nuclei are of a different kind from the other three the secular determinant may be factorised in such a way that the maximum order of any subdeterminant is only two. This means that explicit expressions can be found for all the phosphorus and fluorine transition energies and relative intensities. In order to do this it is necessary to introduce the following auxiliary quantities D_i and θ_i, using the notation described in ref. 2.

[1] Chapman, Paine, Searle, Smith, and White, in the press.
[2] Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," McGraw-Hill, New York, 1959.

$$D_i \sin 2\theta_i = J_{AB}/\sqrt{2},\ i = 1,2\cdots 6$$

$$D_1 \cos 2\theta_1 = \tfrac{1}{2}\nu_0(\sigma_B - \sigma_A) - \tfrac{1}{2}J_{BX} + \tfrac{1}{4}J_{AB} + \tfrac{1}{2}J_{AX}$$
$$D_2 \cos 2\theta_2 = \tfrac{1}{2}\nu_0(\sigma_B - \sigma_A) - \tfrac{1}{2}J_{BX} - \tfrac{1}{4}J_{AB} + \tfrac{1}{2}J_{AX}$$
$$D_3 \cos 2\theta_3 = \tfrac{1}{2}\nu_0(\sigma_B - \sigma_A) + \tfrac{1}{4}J_{AB}$$
$$D_4 \cos 2\theta_4 = \tfrac{1}{2}\nu_0(\sigma_B - \sigma_A) - \tfrac{1}{4}J_{AB}$$
$$D_5 \cos 2\theta_5 = \tfrac{1}{2}\nu_0(\sigma_B - \sigma_A) + \tfrac{1}{2}J_{BX} + \tfrac{1}{4}{}_{BX}J_{AB} - \tfrac{1}{2}J_{AX}$$
$$D_6 \cos 2\theta_6 = \tfrac{1}{2}\nu_0(\sigma_B - \sigma_A) + \tfrac{1}{2}J_{BX} - \tfrac{1}{4}J_{AB} - \tfrac{1}{2}J_{AX}$$

The quantities D_i are usually positive and may always be so chosen but in the present case it is convenient to have the quantities D_1 and D_2 positive and the remainder negative, together with corresponding changes in the signs of the θ_i. This arises because the single phosphorus atom A is more shielded than the two atoms B, that is $\frac{1}{2}\nu_0(\sigma_B - \sigma_A)$ is negative

TABLE 1. *Fluorine transitions in* $P_3N_3Cl_4F_2$.

Transition energies	Relative intensities	Transition energies	Relative intensities
X *transitions relative to* $\nu_0(1-\sigma_X)$ *as origin*		*Combination transitions*	
$-\frac{1}{2}J_{BX} + D_2 - D_4$	$2\cos^2(\theta_2 - \theta_4)$	$\frac{1}{2}J_{BX} - D_3 - D_5$	$2\sin^2(\theta_3 - \theta_5)$
$\frac{1}{2}J_{BX} + D_1 - D_3$	$2\cos^2(\theta_1 - \theta_3)$	$-\frac{1}{2}J_{BX} - D_4 - D_6$	$2\sin^2(\theta_4 - \theta_6)$
$-\frac{1}{2}J_{BX} + D_4 - D_6$	$2\cos^2(\theta_4 - \theta_6)$	$\frac{1}{2}J_{BX} - D_1 - D_2$	$2\sin^2(\theta_1 - \theta_2)$
$\frac{1}{2}J_{AX}$	4	$-\frac{1}{2}J_{BX} + D_2 + D_4$	$2\sin^2(\theta_2 - \theta_4)$
$\frac{1}{2}J_{BX} + D_3 - D_5$	$2\cos^2(\theta_3 - \theta_5)$	$-\frac{1}{2}J_{BX} - D_2 - D_4$	$2\sin^2(\theta_2 - \theta_4)$
$\frac{1}{2}J_{AX} + J_{BX}$	4	$\frac{1}{2}J_{BX} + D_1 + D_3$	$2\sin^2(\theta_1 - \theta_3)$
$-\frac{1}{2}J_{AX} - J_{BX}$	4	$-\frac{1}{2}J_{BX} + D_4 + D_6$	$2\sin^2(\theta_4 - \theta_6)$
$-\frac{1}{2}J_{BX} + D_6 - D_4$	$2\cos^2(\theta_4 - \theta_6)$	$\frac{1}{2}J_{BX} + D_3 + D_5$	$2\sin^2(\theta_3 - \theta_5)$
$-\frac{1}{2}J_{AX}$	4		
$\frac{1}{2}J_{BX} - D_3 + D_5$	$2\cos^2(\theta_3 - \theta_5)$		
$-\frac{1}{2}J_{BX} - D_2 + D_4$	$2\cos^2(\theta_2 - \theta_4)$		
$\frac{1}{2}J_{BX} - D_1 + D_3$	$2\cos^2(\theta_1 - \theta_3)$		

TABLE 2. *Phosphorus transitions in* $P_3N_3Cl_4F_2$.

Transition energies	Relative intensities
A transitions relative to $\nu_0(1-\sigma_A)$	
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} - \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} + D_2$	$(\cos\theta_2 + \sqrt{2}\sin\theta_2)^2$
$\nu_0(\sigma_A - \sigma_B) + J_{BX} + D_1 + D_2$	$[\cos\theta_1\cos\theta_2 + \sqrt{2}\sin(\theta_1 - \theta_2)]^2$
J_{AX}	1
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} + \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} + D_1$	$(\cos\theta_1 - \sqrt{2}\sin\theta_1)^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{4}J_{AB} + D_4$	$2(\cos\theta_4 + \sqrt{2}\sin\theta_4)^2$
0	2
$\nu_0(\sigma_A - \sigma_B) + D_2 + D_4$	$2[\cos\theta_2\cos\theta_4 + \sqrt{2}\sin(\theta_2 - \theta_4)]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{1}{4}J_{AB} + D_3$	$2(\cos\theta_3 - \sqrt{2}\sin\theta_3)^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} - \frac{1}{4}J_{AB} - \frac{1}{2}J_{AX} + D_6$	$(\cos\theta_6 + \sqrt{2}\sin\theta_6)^2$
$-J_{AX}$	1
$\nu_0(\sigma_A - \sigma_B) - J_{BX} + D_5 + D_6$	$[\cos\theta_5\cos\theta_6 + \sqrt{2}\sin(\theta_5 - \theta_6)]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} + \frac{1}{4}J_{AB} - \frac{1}{2}J_{AX} + D_5$	$(\cos\theta_5 - \sqrt{2}\sin\theta_5)^2$
B transitions relative to $\nu_0(1-\sigma_A)$	
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} - \frac{1}{4}J_{AB} - \frac{1}{2}J_{AX} - D_6$	$[\sqrt{2}\cos\theta_6 - \sin\theta_6]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{4}J_{AB} - D_4$	$2[\sqrt{2}\cos\theta_4 - \sin\theta_4]^2$
$\nu_0(\sigma_A - \sigma_B) - J_{BX} + D_6 - D_5$	$[-\sin\theta_5\cos\theta_6 + \sqrt{2}\cos(\theta_5 - \theta_6)]^2$
$\nu_0(\sigma_A - \sigma_B) + D_4 - D_2$	$2[-\sin\theta_2\cos\theta_4 + \sqrt{2}\cos(\theta_2 - \theta_4)]^2$
$\nu_0(\sigma_A - \sigma_B) + J_{BX} + D_2 - D_1$	$[-\sin\theta_1\cos\theta_2 + \sqrt{2}\cos(\theta_1 - \theta_2)]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} - \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} - D_2$	$[\sqrt{2}\cos\theta_2 - \sin\theta_2]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} + \frac{1}{4}J_{AB} - \frac{1}{2}J_{AX} - D_5$	$[\sin\theta_5 + \sqrt{2}\cos\theta_5]^2$
$\nu_0(\sigma_A - \sigma_B) - J_{BX} + D_5 - D_6$	$[\cos\theta_5\sin\theta_6 + \sqrt{2}\cos(\theta_5 - \theta_6)]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{1}{4}J_{AB} - D_3$	$2[\sin\theta_3 + \sqrt{2}\cos\theta_3]^2$
$\nu_0(\sigma_A - \sigma_B) + D_3 - D_4$	$2[\cos\theta_3\sin\theta_4 + \sqrt{2}\cos(\theta_3 - \theta_4)]^2$
$\nu_0(\sigma_A - \sigma_B) + J_{BX} + D_1 - D_3$	$[\cos\theta_1\sin\theta_3 + \sqrt{2}\cos(\theta_1 - \theta_3)]^2$
$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} + \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} - D_1$	$[\sin\theta_1 + \sqrt{2}\cos\theta_1]^2$
Combination transitions	
$\nu_0(\sigma_A - \sigma_B) - J_{BX} - D_5 - D_6$	$[\sqrt{2}\sin(\theta_5 - \theta_6) + \sin\theta_5\sin\theta_6]^2$
$\nu_0(\sigma_A - \sigma_B) - D_3 - D_4$	$2[\sqrt{2}\sin(\theta_3 - \theta_4) + \sin\theta_3\sin\theta_4]^2$
$\nu_0(\sigma_A - \sigma_B) + J_{BX} - D_1 - D_2$	$[\sqrt{2}\sin(\theta_1 - \theta_2) + \sin\theta_1\sin\theta_2]^2$

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and has a magnitude less than that of J_{AX}. With these definitions the angles θ_1 and θ_2 are negative, while the remaining four angles are positive with $0 < |\theta_i| < \pi/2$.

By standard formulæ it is now possible to derive the expressions listed in Tables 1 and 2 for the A, B, and X transition energies and relative intensities. It must be emphasised that the quantities D_i defined above are field-dependent because ν_0 and hence $\nu_0(\sigma_B - \sigma_A)$ are proportional to the strength of the applied magnetic field.

The observed and calculated 12 Mc. phosphorus, 40 Mc. fluorine, and 12 Mc. fluorine spectra are shown in Figs. 2, 3, and 4. It may be seen that in the 12 Mc. fluorine spectrum

FIG. 2. *Observed and calculated phosphorus resonance spectrum of* $P_3N_3Cl_4F_2$ *at* 12 Mc.

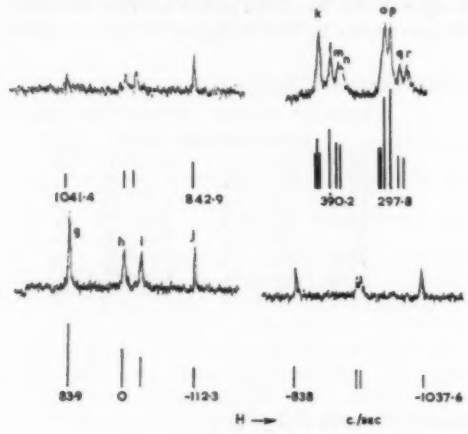
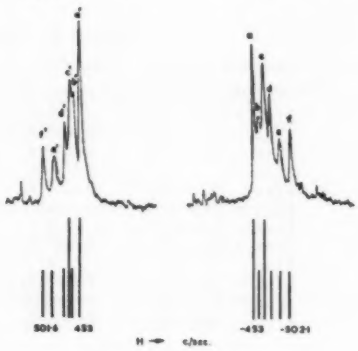


FIG. 3. *Observed and calculated fluorine resonance spectrum of* $P_3N_3Cl_4F_2$ *at* 40 Mc.



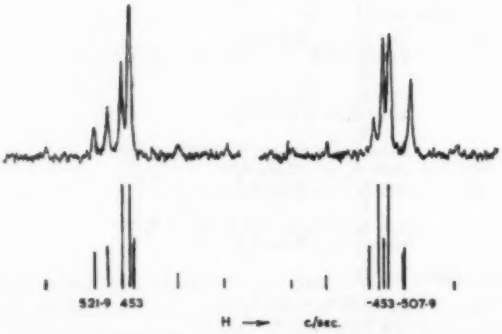


FIG. 4. *Observed and calculated fluorine resonance spectrum of* $P_3N_3Cl_4F_2$ *at* 12 Mc.

there is a marked difference between the high- and the low-field multiplet systems; there is also evidence of a series of low-intensity combination lines.

Analysis and Assignment of the Spectra.—It may be seen from the form of the expressions in Table 1 and the definitions of the quantities D_i that the fluorine transition energies are not very sensitive to small changes in the values of the phosphorus parameters $\nu_0(\sigma_A - \sigma_B)$ (the phosphorus chemical shift) and J_{AB} (the phosphorus–phosphorus spin-coupling constant). By taking account of the known pattern for the system AB_2, it was possible to obtain estimates of the two phosphorus parameters from the phosphorus spectrum obtained at 12 Mc. (7000 gauss). These approximate values were sufficient for use in the calculation of the 40 Mc. (10,000 gauss) fluorine transition energies. In

calculating this fluorine spectrum allowance must be made for the fact that the field-dependent phosphorus chemical shift was determined with a field of 7000 gauss.

From the fluorine transition energies and relative intensities listed in Table 1, it is clear that there are four strong transitions in the fluorine doublet system having intensities approximately twice those of the remaining eight lines. Furthermore, these four transition energies are simply related to the constants J_{AX} and J_{BX}. These strong lines may be readily identified with the lines a, c, a′, and c′ in Fig. 2. This means that the separation ac or a′c′ gives the value of J_{BX}. It is not immediately obvious whether aa′ or cc′ corresponds to the separation $|J_{AX}|$ because the two coupling constants J_{AX} and J_{BX} may have the same or opposite signs. To decide between these two cases use was made of the fluorine spectrum obtained at 12 Mc. (3000 gauss). Although the two fluorine multiplets are almost symmetrical in the 40 Mc. spectrum (they are not quite symmetrical, the separations bc and b′c′ are not the same) the multiplets are quite obviously different in the 12 Mc. spectrum. The reason for this is that the value of the phosphorus chemical shift at this field (3000 gauss) is of the same magnitude as the coupling constant J_{AB} (see below).

The fluorine spectra at both 40 Mc. and 12 Mc. were calculated by using the approximate values of the phosphorus parameters (corrected for changes in the applied field), the observed value of $|J_{BX}|$, and the two alternative values for $|J_{AX}|$. It was possible to account for the fluorine spectra at the two different applied fields only if the signs of J_{AX} and J_{BX} were opposite and further if the sign J_{AB} was opposite to that of J_{AX}. It follows that in the 40 Mc. fluorine spectrum the separation of cc′ gives the value of $|J_{AX}|$, so that either

$$J_{AX} = 934 \text{ c./sec. and } J_{BX} = -14 \text{ c./sec.}$$

or

$$J_{AX} = -934 \text{ c./sec. and } J_{BX} = 14 \text{ c./sec.}$$

By using these exact values of J_{AX} and J_{BX} it was then possible to return to the 12 Mc. phosphorus spectrum and to deduce exact values of $\nu_0(\sigma_A - \sigma_B)$ and $|J_{AB}|$ from the explicit expressions in Table 2. By taking the experimental frequencies for the transitions marked i, j, l, and p the following relations may be derived, with J_{AX} assumed positive and J_{BX} negative:

$$\tfrac{1}{2}\nu_0(\sigma_A - \sigma_B) + \tfrac{3}{4}J_{AB} + D_3 = -113 \text{ c./sec.}$$
$$\nu_0(\sigma_A - \sigma_B) + D_3 + D_4 = -28 \text{ c./sec.}$$
$$\nu_0(\sigma_A - \sigma_B) + D_3 - D_4 = 298 \text{ c./sec.}$$
$$\nu_0(\sigma_A - \sigma_B) + D_4 - D_3 = 390 \text{ c./sec.}$$

These equations, after elimination of D_3 and D_4, lead to the values $\nu_0(\sigma_A - \sigma_B) = 344$ c./sec.; $J_{AB} = -100$ c./sec. If the signs of J_{AX} and J_{BX} were changed simultaneously it would be deduced that $J_{AB} = +100$ c./sec.

Thus to account completely for both sets of fluorine spectra and the phosphorus spectrum it was necessary to assume that the relative signs of the three coupling constants are such that if J_{AX} is of positive sign then both J_{BX} and J_{AB} are of negative sign. It is unusual to be able to determine the relative signs of all spin-coupling constants; the reason why this is possible in the present case may be seen from the explicit expressions in Tables 1 and 2. If the sign of J_{AB} relative to J_{AX} (and hence J_{BX}) be changed it can be seen from Table 2 that the predicted phosphorus spectrum is completely unchanged. This uncertainty in determining the sign of J_{AB} is a property of an AB_2 system.[2] However, the fluorine spectrum will be changed. Consider the six low-field components of the fluorine spectrum, that is, the first six transitions in Table 1. If J_{AB} is replaced by $-J_{AB}$ in the equations defining D_i and θ_i the following relabelling takes place:

$$D_1 \longrightarrow D_2;\ \theta_1 \longrightarrow -\theta_2$$
$$D_3 \longrightarrow D_4;\ \theta_3 \longrightarrow -\theta_4$$
$$D_5 \longrightarrow D_6;\ \theta_5 \longrightarrow -\theta_6$$

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with corresponding changes in the reverse direction, *i.e.*, $D_2 \longrightarrow D_1$, $\theta_2 \longrightarrow -\theta_1$. This means that the six components now have the following forms for their transition energies and relative intensities:

$-\frac{1}{2}J_{BX} + D_1 - D_3$	$2\cos^2(\theta_1 - \theta_3)$
$\frac{1}{2}J_{BX} + D_2 - D_4$	$2\cos^2(\theta_2 - \theta_4)$
$-\frac{1}{2}J_{BX} + D_3 - D_5$	$2\cos^2(\theta_3 - \theta_5)$
$\frac{1}{2}J_{AX}$	4
$\frac{1}{2}J_{BX} + D_4 - D_6$	$2\cos^2(\theta_4 - \theta_6)$
$\frac{1}{2}J_{AX} + J_{BX}$	4

These are not the same expressions as listed in Table 1 (although they are the *negative* of expressions listed in the six high-field components) and they will only give the same predicted fluorine spectrum if $D_1 - D_3$ is equal to $D_2 - D_4$ and $D_4 - D_6$ is equal to $D_3 - D_5$. Similar restrictions would have to be placed on $\theta_1 - \theta_3$ and $\theta_2 - \theta_4$. In fact it is found that at 40 Mc. these conditions are almost met, but at 12 Mc. the quantities $D_1 - D_3$ and $D_2 - D_4$ are significantly different. The values of these quantities, in c./sec., are:

	40 Mc.	12 Mc.
$D_1 - D_3 =$	495·1	501·4
$D_2 - D_4 =$	494·6	514·9
$D_3 - D_5 =$	467·9	455·6
$D_4 - D_6 =$	466·6	441·8

Thus it may be seen that the fluorine spectrum is not independent of the relative signs of J_{AB} and J_{AX}. It is the unsymmetrical nature of the fluorine multiplets, particularly at low fields, that enables one to distinguish between various sign combinations.

By similar reasoning it may be shown that the predicted spectra will be completely unchanged if all three of the coupling constants have their signs changed simultaneously. It is, therefore, possible to obtain only the relative signs of the constants; however, it appears reasonable to assume that the large constant J_{AX}, involving two nuclei directly connected by a single bond, has a positive sign so that the other two constants must be negative.

In the case of an ABX system it has been shown,[2,3] that it is only possible to determine the relative signs of J_{AX} and J_{BX}. However, for an ABC system it is possible to determine the relative signs of all three spin interactions.[4] It is because the X_2 spectrum of an AB_2X_2 system is more complicated than the X spectrum of an ABX system that it is possible to determine the relative signs of all the spin-coupling constants for the former system. For a five-spin system in which the chemical shift $\nu_B - \nu_A$ is much greater than the coupling constant J_{AB} (such a system would not, of course, be classified as an AB_2X_2 system) it would not be possible to determine the relative signs of all the coupling constants.

It has been suggested that the negative sign of coupling constants may be associated with multiple bonding or aromatic character.[5] In this connection it is interesting that the two constants J_{AB} and J_{BX}, which may be negative, involve long-range coupling through the electronic structure of the phosphorus–nitrogen ring system which is currently believed to possess aromatic character.[6]

The final values obtained for the transition energies and relative intensities are listed in Table 3 for the fluorine spectra (at 40 and 12 Mc.) and the phosphorus (12 Mc.) spectrum. These quantities are also shown in Figs. 2—4, from which it may be seen that the agreement between the predicted and the observed spectra is satisfactory. The coupling

[3] Anderson, *Phys. Rev.*, 1956, **102**, 151; Williams and Gutowsky, *J. Chem. Phys.*, 1956, **25**, 1288.
[4] Alexander, *J. Chem. Phys.*, 1958, **28**, 358.
[5] McConnell, *J. Chem. Phys.*, 1959, **30**, 126.
[6] Craig and Paddock, *Nature*, 1958, **181**, 1052.

TABLE 3. *Calculated and observed lines for* $P_3N_3Cl_4F_2$ *(energies in c./sec.).*

Calc. energy	Obs. energy	Relative intensity	Calc. energy	Obs. energy	Relative intensity
	F *resonance at* 40 Mc.			F *resonance at* 12 Mc.	
501·6	501	1·83	521·9	522	1·42
488·1	487	1·83	494·4	495	1·69
473·6	474	1·98	467	467	4·00
467	467	4·00	453	} 453	4·00
460·9	*ca.* 463	1·98	448·8		1·67
453	453	4·00	448·6		1·88
−453	−453	4·00	−434·8	−433	1·67
−459·6	−461	1·98	−453	−453	4·00
−467	−467	4·00	−462·6	−463	1·88
−474·9	−477	1·98	−467	−467	4·00
−487·0	−489	1·83	−507·9	} 507	1·42
−502·1	−502	1·83	−508·4		1·69
		Combination lines			
1022·1	—	0·02	692	—	0·12
938·6	—	0·02	620·8	—	0·33
59·1	—	0·17	349·9	—	0·58
36·6	—	0·17	251	—	0·31
−22·6	—	0·17	−265	—	0·31
−73·1	—	0·17	−335·9	—	0·58
−924·6	—	0·02	−606·8	—	0·33
−1036·1	—	0·02	−706	—	0·12
		P *resonance at* 12 Mc.			
	A *transitions*			B *transitions*	
1041·4	1040	0·71	412	} *ca.* 413	1·84
950·3	948	0·92	410·1		2·67
934	934	1	407·6		1·86
842·9	841	1·37	390·2	390	3·10
83·9	84	3·33	378·5	378	2·37
0	0	2	372·6	372	2·29
−28·4	−28	1·57			
−112·3	−113	1·11	311·6	} ca. 308	2·15
−838	−837	1·16	308·4		2·16
−934	−935	1	306·3		4·89
−941·6	−941	0·98	297·8	298	5·33
−1037·6	−1039	0·86	281·5	282	1·71
			271·5	271	1·64
	Combination lines				
1657	0·001				
716	*ca.* 0·003				
−290	0·001				

constants derived for triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride may be of use in accounting for some of the features of the more complex spectra of the 1,1,3-trifluoride 3,5,5-trichloride and 1,1,3,3-tetrafluoride 5,5-dichloride.[1]

Experimental.—The nuclear magnetic resonance spectra were obtained with a Varian V 4300B high-resolution spectrometer operating at 40 Mc. (approx. 10,000 gauss) and 12 Mc. (approx. 3000 gauss) for fluorine and at 12 Mc. (approx. 7000 gauss) for phosphorus. The pure liquid compound was contained in a 5-mm. sample tube sealed to prevent reaction with atmospheric moisture. The spectra were referenced by the side-band technique.

The authors are grateful to Messrs. Albright and Wilson for the sample of triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride and to Dr. R. J. Abraham for helpful discussions. One of them (M. L. H.) thanks C.S.I.R.O. for an Overseas Post-Graduate Studentship.

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[*Received, August 2nd,* 1960.]

265. *The Thermal Decomposition of Hexafluoroacetone.*

By W. Batey and A. B. Trenwith.

The thermal decomposition of hexafluoroacetone in a steel vessel at temperatures in the range 550—628° is described. At the lower temperatures a first-order reaction leading to the formation of hexafluoroethane and carbon monoxide predominates; this occurs as a result of a rearrangement rather than a free-radical mechanism. At the higher temperatures, a second first-order mode of decomposition to trifluoroacetyl fluoride and difluoromethylene becomes increasingly important and predominates at 600°; at this temperature, difluoromethylene radicals polymerise readily to octafluoroisobutene. Trifluoroacetyl fluoride is more stable than hexafluoroacetone, decomposing to carbonyl fluoride and difluoromethylene. Carbonyl fluoride decomposes by a heterogeneous process to yield mainly carbon monoxide.

Few kinetic studies have been made of the thermal decomposition of completely fluorinated organic compounds, and those by Atkinson and Trenwith,[1] Atkinson and Atkinson,[2] Dresner, Mao, and Young,[3] and Cady [4] indicate that the products are usually appreciably different from those of the analogous hydrocarbons. As yet there is insufficient evidence to allow the mode of decomposition of a perfluoro-compound to be predicted with any certainty, but the present work shows that certain types of reaction appear to be common to quite different systems and so may be characteristic of many perfluoro-compounds.

The pyrolysis of hexafluoroacetone has been followed in a static system with a steel reaction vessel. The products and the rates of reaction show that there are two distinct modes of decomposition; the first is an initial splitting of the molecule into trifluoroacetyl fluoride and a difluoromethylene radical, and the second involves the rearrangement to hexafluoroethane and carbon monoxide which is predominant at lower temperatures. Rate constants for both processes have been determined and compared with available data for similar reactions of other perfluoro-molecules.

Experimental

Materials.—Hexafluoroacetone was prepared by permanganate oxidation of octafluoroisobutene.[5] It was fractionated in a low-temperature (Podbielniak) distillation column, a middle cut being taken for use and stored in a blackened bulb at liquid-nitrogen temperature.

Carbonyl fluoride was prepared by the action of silver difluoride on carbon monoxide.[6]

The purity of these materials was checked by molecular-weight determinations and by their infrared spectra, which corresponded with those given by Simons.[7]

Apparatus.—This was of the conventional static type; a mild spun-steel reaction vessel (25 × 6·5 cm.) with a capillary inlet and a thermocouple well was joined to the glass part of the apparatus by a Fyffe coupling and Neoprene ring. It was heated in a tubular electric furnace kept to within ±0·2° of the required temperature by a " Sunvic " resistance-thermometer controller, type R.T.2. The temperature was measured by means of a chromel–alumel thermocouple and a Doran potentiometer. Evacuation of the apparatus was by a mercury-vapour pump backed by a rotary oil pump. A constant-volume mercury manometer [8] was used to measure pressures in the reaction vessel. A two-way tap enabled it to be connected to either a storage bulb or a series of four collecting traps; the first three traps were empty and the last contained activated charcoal. The empty traps were connected to a small Podbielniak-type

[1] B. Atkinson and Trenwith, *J.*, 1953, 2082.
[2] B. Atkinson and V. Atkinson, *J.*, 1957, 2086.
[3] Dresdner, Mao, and Young, *J. Org. Chem.*, 1959, **24**, 698.
[4] Cady, *Proc. Chem. Soc.*, 1960, 133.
[5] Morse, Ayscough, and Leitch, *Canad. J. Chem.*, 1955, **33**, 453.
[6] Ruff and Miltschitzky, *Z. anorg. Chem.*, 1934, **221**, 154.
[7] Simons, " Fluorine Chemistry," Academic Press Inc., New York, 1954, Vol. II.
[8] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, p. 122.

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distillation column, and the charcoal trap to a gas burette which could be used as either a Töpler pump or a McLeod gauge.

Operation.—The reaction vessel was first heated to 700° with a stream of hydrogen passing through it to remove any oxide scale formed during welding. A capillary outlet provided for this purpose was subsequently sealed off. The vessel was then filled with hexafluoroacetone and left overnight at 600° to condition the surface.

The decomposition of hexafluoroacetone was followed by both the change of pressure with time and an analysis of the products after various periods of heating. Pressure–time measurements were made in the usual way, pressures being noted approximately every half-minute, and initial pressures were determined by extrapolation of the pressure–time curves to zero time. Between runs the reaction vessel was evacuated for at least 15 min. Results for duplicate runs showed good reproducibility. For analysis, five identical runs were made for each heating period and the products combined to give sufficient material for the distillations. The four collecting traps were cooled in liquid nitrogen, condensable products being frozen in the first three traps and non-condensable materials adsorbed on the activated charcoal. The condensable material was transferred to the low-temperature column and analysed by fractional distillation, individual fractions being identified by their b. p., molecular weight, and infrared spectrum. The non-condensable portion was transferred to the gas-burette by raising the temperature of the charcoal to 300°, and measured; its composition was ascertained by molecular-weight measurements and analysis by mass spectrometer.

Results

The compounds identified in the products of pyrolysis of hexafluoroacetone were trifluoroacetyl fluoride, octafluoroisobutene, hexafluoroethane, carbonyl fluoride, and carbon monoxide; their amounts after various heating times at 600° are shown in Fig. 1. Carbonyl fluoride was present in measurable quantities only after the time required for about 50% decomposition. Rate measurements were made at temperatures between 550° and 628°. In the lower-temperature range pressure changes were very slow and just measurable manometrically, and at the higher were extremely rapid. At each temperature, the initial rates, given by the initial

TABLE 1. *Variation of first-order rate constant with pressure and temperature.**

Temp.	550°		567°		576°		590°
p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$
31·5	0·635	55·5	1·207	55·5	1·891	51·0	3·920
46·0	0·652	60·5	1·256	64·5	1·891	59·5	3·948
62·0	0·645	65·0	1·246	71·5	1·790	69·5	3·960
		76·0	1·210	75·5	1·880	77·5	3·935
		84·0	1·202	85·5	1·905	84·0	3·868
		90·5	1·214	94·5	1·820	94·0	3·710
				103·0	1·748	102·0	3·871
Mean	0·645		1·223		1·846		3·887

Temp.	596°		610°		628°
p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$
54·5	5·685	42·5	11·76	46·0	26·96
60·5	5·617	51·5	11·85	62·5	27·52
70·0	5·712	61·0	11·96		
84·5	5·678	72·0	12·22		
96·0	5·830	79·0	11·65		
109·5	5·569	90·0	11·78		
Mean	5·682		11·87		27·24

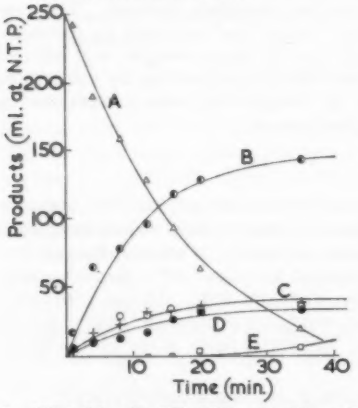
* Pressures (p_0) are in mm. of Hg. Rates $(dp/dt)_0$ are in mm. of Hg/sec.

slopes of the pressure–time curves, were determined for initial pressures of hexafluoroacetone between 30 and 110 mm. Plots of initial rate against pressure of hexafluoroacetone for every temperature gave straight lines passing through the origin and indicated that a first-order rate law applies to the decomposition under the experimental conditions. Values obtained for the

first-order rate constants at various pressures and temperatures are given in the Table. The Arrhenius plot of the rate constants is shown in Fig. 2. The points deviate from a straight line at the lower temperatures, the deviation increasing as the temperature falls. The temperature-dependence of the first-order rate constant is $k = 10^{16\cdot6}$ exp $(-79{,}100/\boldsymbol{R}T)$ sec.$^{-1}$ from the full line and $k' = 10^{9\cdot6}$ exp $(-50{,}900/\boldsymbol{R}T)$ sec.$^{-1}$ from the broken line.

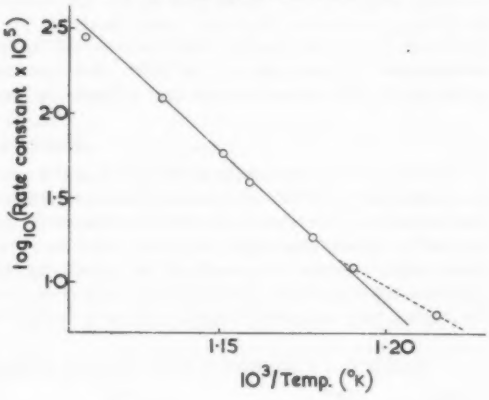
The decomposition of carbonyl fluoride was also investigated. There was no change in pressure when this compound was heated. At 600°, the products were carbon monoxide and a trace of silicon tetrafluoride. The rate of decomposition was followed between 554° and 600°. At the different temperatures a fixed amount was heated for varying times and the carbon monoxide was measured. Initial slopes of the curves for carbon monoxide formed against time were determined and graphs plotted of dCO/dt against the initial pressures of carbonyl

FIG. 1. *Products of pyrolysis of hexafluoroacetone at 600°.*



A, $(CF_3)_2CO$. B, $CF_3{\cdot}COF$. C, CO and C_2F_6 (+ = CO, ○ = C_2F_6). D, C_4F_8. E, COF_2.

FIG. 2. *Arrhenius plot of the rate constants for the decomposition of hexafluoroacetone.*



fluoride. These were straight lines passing through the origin. An Arrhenius plot of the first-order rate constants derived from the slopes of these lines yielded the rate expression $k'' = 10^{13\cdot3}$ exp $(-62{,}700/\boldsymbol{R}T)$ sec.$^{-1}$.

Some trifluoroacetyl fluoride, separated from combined products of pyrolysis by fractional distillation, was heated in the reaction vessel at 600°; it gave a very slow, steady increase in pressure with time. After 15 minutes' heating, the products consisted of carbonyl fluoride, octafluoroisobutene and carbon monoxide; there was some unchanged material. Even after being heated at 600° for >4 hours, some of the trifluoroacetyl fluoride remained undecomposed.

DISCUSSION

Trifluoroacetyl fluoride is the major product of pyrolysis of hexafluoroacetone at 600°. To account for its formation, it is suggested that a primary step in the decomposition is

$$CF_3{\cdot}CO{\cdot}CF_3 = CF_3{\cdot}COF + CF_3^{\bullet} \quad \ldots\ldots\ldots\ldots (1)$$

followed by

$$2CF_3^{\bullet} = C_2F_4 \quad \ldots\ldots\ldots\ldots (2)$$

Atkinson and Atkinson [2] have shown that at 650°, tetrafluoroethylene decomposes to give octafluoroisobutene, with octafluorocyclobutane and hexafluoropropene as intermediates. The tetrafluoroethylene and octafluorocyclobutane are rapidly consumed but the hexafluoropropene disappears much more slowly. The octafluoroisobutene formed in the hexafluoroacetone decomposition almost certainly results from the decomposition of

tetrafluoroethylene produced by reactions (1) and (2). As would be expected, it is always approximately one quarter of the amount of trifluoroacetyl fluoride formed. Of the intermediates, tetrafluoroethylene and octafluorocyclobutane could not be produced in measurable quantities because of their obvious instability at 600°. Hexafluoropropene, if formed, would have been separated in the hexafluoroacetone fraction because of the identity of boiling points; but since the latter must always be present in excess, it is understandable that the former was not detected from the infrared spectra.

If the steps leading to the formation of octafluoroisobutene from difluoromethylene radicals are rapid compared with (1), the rate of the overall reaction

$$CF_3{\cdot}CO{\cdot}CF_3 = CF_3{\cdot}COF + \tfrac{1}{4}C_4F_8 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

will equal that of reaction (1). The measured constant k is considered to be the rate constant for the reaction (3) because it applies between 576° and 628°. Since, in reaction (3), $-\mathrm{d}CF_3{\cdot}CO{\cdot}CF_3/\mathrm{d}t = 4\mathrm{d}p/\mathrm{d}t$, the rate constant k_1 for (1) will be four times k; hence $k_1 = 10^{17.2} \exp(-79{,}100/RT)$ sec.$^{-1}$.

Reaction (1) may be considered to occur by transfer of a fluorine atom from one carbon to the next and splitting-off of the remaining difluoromethylene group. (The high A factor seems to indicate two or more successive steps.)

It is pertinent to consider other reactions which appear to involve a similar initial process. One such is the decomposition of hexafluoropropene for which the proposed primary step [2] is

$$CF_3{\cdot}CF{:}CF_2 = CF_3{\cdot}{:}CF_2 + CF_2{:}$$

This reaction has an activation energy of $\leqslant 75$ kcal. mole^{-1}, significantly close to that found for (1). Steunenberg and Cady [9] have suggested that a number of saturated fluorocarbons may also decompose by a process with a similar initial step; thus, for instance, the products of decomposition of octafluoropropane indicate that the most likely primary step is

$$CF_3{\cdot}CF_2{\cdot}CF_3 = CF_3{\cdot}CF_2 + CF_2{:}$$

Although a detailed study of the decomposition of trifluoroacetyl fluoride has not been made, it seems reasonable to assume from the products that the initial step in the decomposition is

$$CF_3{\cdot}COF = COF_2 + CF_2{:}$$

The apparently greater thermal stability of this compound than of hexafluoroacetone is analogous to the greater stability of hexafluoroethane than of octafluoropropane.[9] By further analogy, perfluoroisobutene might be expected to decompose and to yield only perfluoro-olefins, following the initial reaction

$$(CF_3)_2C{:}CF_2 = CF_3{\cdot}CF{:}CF_2 + CF_2{:}$$

In fact, it is comparatively stable at 600° and decomposes at higher temperatures to give one molecule of hexafluoroacetone for each molecule decomposing, the proposed initial reaction being

$$(CF_3)_2C{:}CF_2 = CF_3{\cdot}CF{:}CF{\cdot} + CF_3{\cdot}$$

Another molecule which does not decompose in the expected manner is perfluorodiethyl ether, since no perfluoroethyl trifluoromethyl ether was found among the products.[3] It is of interest that all the perfluoro-compounds which decompose readily by a process involving the initial step we have been considering possess three linked carbon atoms per molecule. Although there appears to be no theoretical significance in this, it would be of interest to see whether other similar fluoro-compounds exhibit the same behaviour.

[9] Steunenberg and Cady, *J. Amer. Chem. Soc.*, 1952, **74**, 4165.

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To account for the formation of hexafluoroethane and carbon monoxide from hexafluoroacetone it is suggested that there is a second mode of decomposition, namely:

$$CF_3{\cdot}CO{\cdot}CF_3 = CO + C_2F_6 \quad \ldots\ldots\ldots\ldots \quad (4)$$

This reaction is predominant at temperatures below 570° and the one to which the rate constant k' applies. Since for it $-dCF_3{\cdot}CO{\cdot}CF_3/dt = dp/dt$, k_4 equals k'. The reaction could occur by a chain mechanism with $CF_3{\cdot}$ and $CO{\cdot}CF_3{\cdot}$ radicals as intermediates, or by a rearrangement involving the formation of an activated complex with a three-membered carbon ring. The latter is preferred in view of the low A factor which indicates the negative entropy of activation associated with the formation of a cyclic intermediate. A somewhat similar rearrangement through a cyclic intermediate probably occurs in the decomposition of perfluoroethyl ether, where, as a primary step, the splitting of the molecule into carbonyl fluoride and octafluorobutane has been proposed.[3]

The thesis of two possible modes of decomposition of hexafluoroacetone can be tested in the following way. Since $dCF_3{\cdot}COF/dt = k_1[CF_3{\cdot}CO{\cdot}CF_3]$ and $dCO/dt = k_4[CF_3{\cdot}CO{\cdot}CF_3]$ it follows that $dCO/dCF_3{\cdot}COF = k_4/k_1$. The ratio of the rate constants at 600° is 0·29 and this agrees well with the 0·30 found for $dCO/dCF_3{\cdot}COF$ from the initial slopes of the appropriate curves in Fig. 1.

The fact that only carbon monoxide, silicon tetrafluoride, and unchanged material were present in the products of pyrolysis of carbonyl fluoride indicates the occurrence of some reaction with the surface of the vessel. This view is supported by the comparatively low energy of activation found, since the reaction must involve the initial splitting of a C–F bond, and this process requires [10] an energy of about 116 kcal. mole^{-1}.

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[10] Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958.

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266. *Catalysis by Hydrogen Halides in the Gas Phase. Part V.*[1] *t-Pentyl Alcohol and Hydrogen Chloride.*

By V. R. STIMSON and E. J. WATSON.

A homogeneous, gas-phase, molecular decomposition of t-pentyl alcohol into 2-methylbut-2- and -1-ene, 3-methylbut-1-ene, and water, catalysed by hydrogen chloride in the temperature range 370—503°, is described.

HYDROGEN BROMIDE and hydrogen chloride catalyse the gas-phase dehydration of t-butyl alcohol at 315—422° and 328—454° respectively.[1] The similar dehydration of t-pentyl alcohol catalysed by hydrogen bromide [1] occurs at 308—415°. This reaction, catalysed by hydrogen chloride, is now described.

EXPERIMENTAL

The materials used and experimental procedures have been described in previous Parts.[1] As only a small correction for the equilibrium between pentenes and hydrogen chloride was necessary in the study [2] of the decomposition of t-pentyl chloride at 270—326°, it was neglected in the present work; $p_t/p_0 = 1{\cdot}91 \pm 0{\cdot}03$ (20 values). As t-pentyl alcohol undergoes uncatalysed decomposition [3] at a measurable rate above 480°, a small correction for this (*ca.* 10%) was made to the catalysed rates at 496° and 503°, where $t_{0.5} < 5$ min. Under our conditions

[1] Parts I, II, III, and IV, *J.*, 1960, 2836, 3087, 3090, 3920.
[2] Brearley, Kistiakowsky, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 43.
[3] Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395.

at 496° $10^3k_1 = 0{\cdot}27$ sec.$^{-1}$ for the uncatalysed reaction, a value slightly lower than that found by Schultz and Kistiakowsky.[3]

Although cyclohexene is a more effective inhibitor than propene,[4] it cannot be used above *ca.* 440° where its own decomposition commences. It was accordingly used at 439° and propene was used at 450° and 475°.

Products.—In two experiments t-pentyl alcohol (233 mm., 124 mg.; 251 mm., 134 mg.) and hydrogen chloride (106, 114 mm.) reacted to completion at 439°, giving $10^7k_1/p_{HCl} = 58$, 57 sec.$^{-1}$ mm.$^{-1}$ respectively. The products were expanded directly into a 5-l. bulb containing magnesium perchlorate and calcium hydroxide. After *ca.* 15 min., the remaining gas was trapped and weighed (Found: 94, 109 mg. Theor. as pentene: 99, 107 mg.). The proportions of the various pentenes were estimated by gas chromatography within *ca.* 5% as described in Part IV [1] (Found: 2-methylbut-2-ene, 67, 70%; 2-methylbut-1-ene, 31, 28%; and 3-methylbut-1-ene, 2, 2%). The three methylbutenes were found in approximately similar proportions in several other experiments at various temperatures. The temperatures used did not cause the cracking of these hydrocarbons, for which 500—600° appears to be necessary. Retention times were identical with those of authentic samples and different from those of pent-1-ene and *cis*- and *trans*-pent-2-ene made from pentan-2-ol.

t-Pentyl alcohol (225 mm., 1·30 mmoles) and hydrogen chloride (60 mm.) reacted to completion at 475°. The products were separated at −80° and water, whose microanalysis showed very little carbon and chlorine, was estimated after adsorption on a drying agent (Found: 1·32 mmole).

Isomerisation of Methylbutenes.—2-Methylbut-2-ene (129 mm.) and hydrogen chloride (42 mm.) reacted at 393° for 3 hr. After removal of hydrogen chloride with magnesium perchlorate and calcium hydroxide as above the products were: 2-methylbut-2-ene 70%, 2-methylbut-1-ene 25%, and 3-methylbut-1-ene 5%. On similar treatment 2-methylbut-1-ene (148 mm.) and hydrogen chloride (101 mm.) gave 2-methylbut-2-ene 68%, 2-methylbut-1-ene 29%, and 3-methylbut-1-ene 3%. In similar experiments without hydrogen chloride no change of 2-methylbut-2- or -1-ene was found. The above compositions evidently correspond to that at equilibrium, as the equilibrium composition at 393° (see Part IV) calculated from tabulated data [5] is: 2-methylbut-2-ene 59·7%, 2-methylbut-1-ene 35·9%, and 3-methylbut-1-ene 4·4%. Considerable uncertainty attaches to these data which are based on incomplete spectroscopic measurements.[6]

Results and Discussion

Whereas the uncatalysed decomposition of t-pentyl alcohol occurs only above *ca.* 480°, in the presence of hydrogen chloride pentenes and water are produced at measurable rates at 370—503° (Table 2), in a reaction apparently analogous to that with hydrogen bromide [1] at 308—415°, namely: $CMe_2Et{\cdot}OH + HCl \longrightarrow C_5H_{10} + H_2O + HCl$. No gas uncondensed in liquid air or lower hydrocarbon was detected. The rate follows the

Table 1. *Variation of rate at 410° with pressure of hydrogen chloride.*

p_{HCl} (mm.)	p_{ROH} (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	p_{HCl} (mm.)	p_{ROH} (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	p_{HCl} (mm.)	p_{ROH} (mm.)	10^5k_1 (sec.$^{-1}$)	$10^7k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
63	92	12·6	20·0	168	126	33	19·7	235	97	48	20·4
76	237	15·5	20·4	194	167	34	17·6	287	138	58	20·2
97	207	19·4	20·0	196	163	36	18·4	398	89	73	18·3
109	344	23·0	21·1	208	137	42	20·2			Mean	19·8 ± 0·6
133	85	27	20·3	215	103	45	20·9				

relation, $-d[ROH]/dt = k_2[ROH][HCl]$; *i.e.*, since [HCl] remains constant, individual runs are of the first order. At 410° the first-order rate constants are proportional to p_{HCl} for initial pressures of 63—398 mm. of hydrogen chloride and 85—344 mm. of t-pentyl

[4] Maccoll and Thomas, *J.*, 1957, 5033.
[5] Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.
[6] Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559.

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alcohol (Table 1). The Arrhenius equation $k_2 = 6{\cdot}7 \times 10^{12} \exp(-34{,}000/RT)$ (sec.$^{-1}$ c.c. mole^{-1}) describes the rate between 370° and 503°.

At 410° the rate of catalysis by hydrogen bromide is 27 times that with hydrogen chloride, and this ratio is approximately the value of their relative catalytic powers in the other cases so far studied. It also agrees with their approximate relative catalytic effects (20—40 : 1) on the decomposition of acetaldehyde and that predicted from the

TABLE 2. *Variation of rate with temperature.*

Temp.	503·9°	496·2°	486·6°	475·0°	463·6°	450·2°	439·2°	410·0°	370·3°
No. of runs	4	5	7	8	7	10	19	13	4
$10^7 k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)	330	270	220	175	115	85	57	19·8	4·3
k_1/p_{HCl} (sec.$^{-1}$ c.c. mole^{-1})	1620	1300	1050	820	530	384	254	85	17·2

TABLE 3. *Rates with added cyclohexene at 439° and propene at 450° and 475°.*

Temp.	No. of runs	$p_{C_6H_{10}}$ (mm.)	p_{HCl} (mm.)	p_{ROH} (mm.)	$10^7 k_1/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$)
439°	6	43—300	129—202	117—192	54 ± 4
		$p_{C_3H_6}$			
450	7	9—356	94—185	104—194	91 ± 7
475	7	29—280	50—132	86—237	180 ± 9

TABLE 4. *Rates in packed vessels,* $10^7 k/p_{HCl}$ (sec.$^{-1}$ mm.$^{-1}$).

Temp.	S/V 1·0 cm.$^{-1}$	S/V 3·6 cm.$^{-1}$	No. of runs	S/V 9 cm.$^{-1}$	No. of runs
370°	4·3	5·6 ± 0·4	6	6·8 ± 0·5	5
410	19·7	23 ± 1	7	26 ± 1	5
450	82	94 ± 2	7	100 ± 9	7

energies of gas-phase heterolytic dissociation of the hydrogen halides.[7] As for t-butyl alcohol, the activation energy for the reaction with hydrogen chloride is a few kcal. higher than with hydrogen bromide.

As increase of the surface : volume ratio of the reaction vessel does not significantly affect the rate (Table 4), the reaction is considered to be homogeneous. Indications that a heterogeneous reaction also occurs at *ca.* 340° were noted but not investigated; this behaviour has also been found in the cases of other alcohols.[1] As no induction periods were observed, and additions of up to 300 mm. of cyclohexene or propene, effective inhibitors of free-radical chains in similar systems,[4] had no effect on the rate (Table 3), the reaction is believed to be molecular.

The pentenes produced are 2-methylbut-2- and -1-ene, and 3-methylbut-1-ene in approximately their equilibrium proportions. Whereas the first two are usually found

TABEL 5. *Comparative rates of gas-phase reactions of t-pentyl and t-butyl compounds.*

Reaction	Temp.	Factor	Ref.
Uncatalysed dehydrn. of alcohols	505°	2·3	3
Dehydrochlorin. of chlorides	313	2·2	2
Dehydrobromin. of bromides	240	3·2	*
Elimin. of AcOH from acetates	260	1·4	8
Dehydrn. of alcohols catalysed by HBr	315—383	2·0	1
Dehydrn. of alcohols catalysed by HCl	340—440	1·5	1

* Harden and Maccoll, *J.*, 1955, 2454; Harden, *J.*, 1957, 5024.

in the decompositions of t-pentyl compounds, the third must have been produced subsequently, presumably by catalysed isomerisation which occurs in our conditions. This may also account for the proportions. Preliminary measurements on the rate of isomerisation show that it is comparable with that of the decomposition, so that the proportion in which the pentenes are produced initially is not known.

[7] Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 474.

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The rate is 1·4—1·5 times as fast as that of the corresponding reaction of t-butyl alcohol. Evidently the effect of substitution at the β-carbon atom is much smaller than that produced by substitution at the α-carbon atom [1] where the rate increases by a factor of *ca.* 60. The relative rates of the gas-phase reactions of t-pentyl and t-butyl compounds that are known to be homogeneous, molecular reactions are listed in Table 5. In all cases the t-pentyl compound reacts faster by a factor of *ca.* 2. In view of the quite different types of mechanism proposed for the decompositions of the alkyl halides and acetates [8] no conclusions about the mechanism of the catalysed reactions can be drawn by use of analogy.

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[*Received, October 3rd*, 1960.]

[8] Maccoll, " Theoretical Organic Chemistry," Butterworths, London, 1959, p. 230.

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267. *Steric Effects in Di- and Tri-arylmethanes. Part IV.*[1] *Electronic Absorption Spectra of α-Alkyl Derivatives of Michler's Hydrol Blue.*

By C. C. BARKER and G. HALLAS.

Absorption spectra of α-alkyl derivatives of Michler's Hydrol Blue (I; R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, and Bu^t) have been determined for solutions in 98% acetic acid. The spectra of dimeric derivatives formed during 1—4 days in this solvent have also been determined and are discussed in terms of molecular conformation.

IT was pointed out in Part III [1] of this series that the bathochromic shift of 13·5 mμ observed on passing from Michler's Hydrol Blue (I; R = H) to Malachite Green (I; R = Ph) was caused by combined electronic and steric effects of the phenyl group. In the hope that the simpler electronic effect of an alkyl group would make analysis of the spectral shifts easier, the α-alkyl derivatives of Michler's Hydrol Blue were examined. The $-E$ activity of an α-alkyl group produces a hypsochormic shift whereas the expected steric effect is bathochromic.

Michler's Hydrol Blue gives an intense first band followed by a weak second band with two peaks (Table), but the α-t-butyl derivative gives first and second bands of low

Absorption maxima (mμ) ($10^{-4}\varepsilon$ *in parentheses*) *of derivatives of Michler's Hydrol Blue in* 98% *acetic acid.*

Michler's Hydrol Blue α-subst.	Fresh solution	Solution after *n* hr.	*n*
None	607·5 (14·75); 390 (0·45); 368·5 (0·50)		
Me	606 (1·09); 397·5 (0·10); 376 (0·08)		
Et	620 (1·90); 402·5 (0·21); 381 (0·17)	637·5 (0·86); 350 (1·48)	24
Pr^n	620 (1·04); 402·5 (0·18); 382·5 (0·16)	638 (1·23); 347·5 (1·29)	24
Pr^i	610 (1·41); 402 (0·20); 382·5 (0·17)	630 (0·07); 353 (0·26)	75
Bu^n	617·5 (0·41); [a] 402 (0·07); 381 (0·06)	638 (0·95); 346 (1·42)	60
Bu^i	610 (1·27); 402·5 (0·25); 383 (0·17)	637·5 (0·46; 346 (1·05)	95
Bu^t	617·5 (0·064); 384 (0·077);		

[a] Increased to 0·93 during 1 hr.

but similar intensity, and the second band shows only a single peak (Table). Further, although addition of hydrochloric acid to a solution of Michler's Hydrol Blue in 98% acetic acid leads to progressive disappearance of both these bands by formation of the bivalent ion (II), addition of hydrochloric acid to the α-t-butyl derivative leads to preferential reduction of the first band and it is assumed that this band arises from the

[1] Part III, *J.*, 1961, 1285.

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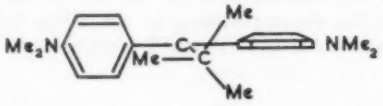
univalent ion (I; R = Bu^t) and that the second band arises from the bivalent ion (III; R = Bu^t). There is no spectral evidence to indicate formation of the bivalent ion (III; R = H) from Michler's Hydrol Blue, and the ready formation of this type of ion from the α-t-butyl derivative can be explained by assuming that the t-butyl group causes rotation of one only of the dimethylaminophenyl groups about a central bond (see Figure).



The molecular conformation of the α-t-butyl derivative of Michler's Hydrol Blue.

The resulting unsymmetrical conformation would produce two effects. First, the incompletely conjugated nitrogen atom would be protonated readily. Second, the univalent cation (I; R = Bu^t) would become electronically unsymmetrical. It is well established that by twisting the aryl nuclei about the central bonds of an electronically symmetrical cyanine a bathochromic shift is produced, whereas in an electronically unsymmetrical cyanine the shift is hypsochromic,[2] so that the effect of twisting one of the dimethylaminophenyl groups about a central bond would be to produce a bathochromic shift which with increased rotation of the aryl group would decrease and ultimately become hypsochromic. The bathochromic shift of 10 mμ brought about by the α-t-butyl group is significantly smaller than the shift of 42 mμ shown by the 2,6,2′,6′-tetramethyl derivative [3] and is consistent with the production of an unsymmetrical conformation by the t-butyl group. This argument ignores the purely electronic effect of the t-butyl and methyl groups, but these groups in the 4-position of Malachite Green produce hypsochromic shifts of only 5 and 4·5 mμ respectively.[1]

$Me_2N{\cdot}C_6H_4{\cdot}CR{:}C_6H_4{:}NMe_2^+$ (I)

$^+Me_2HN{\cdot}C_6H_4{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NHMe_2^+$ (II)

$^+Me_2HN{\cdot}C_6H_4{\cdot}CR{:}C_6H_4{:}NMe_2^+$ (III)

$Me_2N{\cdot}C_6H_4{\cdot}C(=CRR'){\cdot}C_6H_4{\cdot}NMe_2$ (IV)

$^+Me_2N{:}C_6H_4{=}C{\cdot}CRR'{\cdot}C(C_6H_4{\cdot}NMe_2)_2$ / $Me_2N{\cdot}C_6H_4$; CHRR′ (V)

$^+Me_2N{:}C_6H_4{=}C{\cdot}CRR'{\cdot}C(C_6H_4{\cdot}NMe_2)_2$ / $^+Me_2HN{:}C_6H_4$; CHRR′ (VI)

(All substituents in aromatic rings are *para*.)

The low intensity of the first band of the α-t-butyl derivative also points to a lack of electronic symmetry which reduces the resonance energy of the ion (I; R = Bu^t) and thus moves the dye base–dye equilibrium in favour of the dye base. The presence of large amounts of dye base (or protonated dye base) in an ethanolic solution of the monohydrochloride of the α-t-butyl derivative is confirmed by the presence of an intense band at 262·5 mμ.

Indirect support for the unsymmetrical conformation of the α-t-butyl derivative of Michler's Hydrol Blue is provided by a study of other α-alkyl derivatives. In general, the bases of these compounds very readily form an olefin (IV) by loss of water, particularly in acid solution, so that in acetic acid the equilibrium is between olefin and the ion (I) and there is no change in hybridisation at the central carbon atom; it is the release of compressional energy upon changing the valency distribution of the central carbon atom of Michler's Hydrol from tetrahedral to trigonal that assists the formation of Michler's Hydrol Blue. Consequently, α-alkyl derivatives of Michler's Hydrol Blue give weak absorption bands in acetic acid.

A freshly prepared solution of the α-ethyl derivative of Michler's Hydrol Blue in 98% acetic acid gives absorption bands which, apart from their low intensity, are very similar

[2] Brooker, White, Sprague, Dent, jun., and van Zandt, *Chem. Rev.*, 1947, **41**, 325.
[3] Barker, Bride, and Stamp, *J.*, 1959, 3957.

to those of the parent compound. The bathochromic shift (12·5 mμ) of the first band relative to that of Michler's Hydrol Blue reveals a steric effect apparently greater than that produced by the α-t-butyl group (10 mμ), which is consistent with the unsymmetrical conformation of the t-butyl derivative. However, the spectrum of the α-ethyl derivative in 98% acetic acid changes with time and finally (24 hr.) develops a strong band at 350 mμ (Table). Further, increasing the acidity of the solution by addition of water causes preferential reduction in the intensity of the long-wavelength band, so that two molecular species must be present in solution. This result is consistent with slow dimerisation of the olefin (IV; R = H, R′ = Me) to give a mixture of the ions (V and VI; R = H, R′ = Me). 1,1-Diphenylethylene polymerises to 1,1,3,3-tetraphenylbut-1-ene in the presence of cationic catalysts,[4] and the dimethylamino-groups in the olefin (IV) should facilitate polymerisation. The shift from 620 to 637·5 mμ shown by the first band corresponds to increased crowding in the ion (V; R = H, R′ = Me) compared with the ion (I; R = Et), and it must be assumed that, although the disposition of the dimethylaminophenyl groups is sufficiently unsymmetrical to permit formation of the protonated ion (VI; R = H, R′ = Me), the departure from symmetry is small enough for deviation from planarity to produce a marked bathochromic shift. The position of the band due to the protonated ion (VI; R = H, R′ = Me) at 350 mμ instead of at 384 mμ as in the ion (III; R = Bu^t) is consistent with a hypsochromic shift brought about by twisting the conjugated dimethylaminophenyl group about the central bond, that is, consistent with greater symmetry in the ion (VI; R = H, R′ = Me) and therefore ion (V; R = H, R′ = Me) than in ions (III and I; R = Bu^t).

Very similar behaviour is shown by the propyl, isopropyl, butyl, and isobutyl derivative of Michler's Hydrol Blue (Table). The variations in position of the first band of the monomeric ion (I) must be a function of the $-E$ activity and the steric effect of the alkyl groups, but correlation of these factors with the observed shifts is not possible. The dimeric ions (V) give first bands of essentially constant wavelength with the exception of the isopropyl derivative which gives a very weak band at somewhat shorter wavelength (Table). This dimer is also exceptionally crowded; it has a quaternary β-carbon atom and thus resembles the α-t-butyl derivative of Michler's Hydrol Blue. The bands corresponding to the protonated dimeric ion (VI) also occur at essentially the same position, but again the isopropyl derivative (VI; R = R′ = Me) gives a somewhat weaker band.

The α-methyl derivative is unique in that in acetic acid its spectrum, which closely resembles that of the parent compound, shows no change with time, implying that the dimer is not formed. This interpretation is not in accord with the fact that the β-carbon atom of this dimer carries only a single substituent so that crowding is at a minimum and dimer formation should take place most readily. When a solution of 1,1-bis-(*p*-dimethylaminophenyl)ethylene in acetic acid was kept for 48 hours and then poured into ice-cold, aqueous sodium hydroxide, the dimer was isolated, whereas addition of alkali to the dimer in acetic acid yielded only monomer, and dimer could not be isolated from a solution of monomer in acetic acid that had been kept for only 20 minutes. The dimer sublimed slowly at 200° (bath/10^{-4} mm.) without depolymerising and gave a molecular weight of 465 (micro-Rast) (theor. 532). Clearly, if preceding views about the relation between molecular conformation and the spectra of the dimers are correct, the single substituent on the β-carbon of this dimer (V; R = R′ = H) provides insufficient hindrance to stabilise the protonated dimer (VI; R = R′ = H) so that the spectrum of the dimer closely resembles that of the parent monomer.

Preparations.—The interaction of the appropriate alkyl-lithium compound with Michler's ketone gave the α-ethyl, α-propyl, α-butyl, and α-isobutyl derivatives of Michler's Hydrol as compounds that crystallised from ethanol containing a trace of sodium hydroxide; in the absence of base, water is readily eliminated, yielding the olefin. Both the olefin and the alcohol are satisfactory precursors of the corresponding derivative of Michler's

[4] Evans, Jones, and Thomas, *J.*, 1955, 1824.

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Hydrol Blue. The α-ethyl derivative was known,[5] and the α-methyl derivative could only be isolated as the known olefin.[6] The isopropyl derivative was obtained through the more easily prepared Grignard reagent, the product from which was isolated by treatment with aqueous ammonium chloride and therefore obtained as the olefin, m. p. 95—96°; Lemoult [7] gives m. p. 88°.

The α-t-butyl derivative, m. p. 149—150°, previously prepared through t-butylmagnesium chloride by Madelung and Völker [8] who give m. p. 147°, was obtained from *p*-dimethylaminophenyl-lithium and methyl pivalate, this method avoiding the difficult [9] preparation of t-butyl-lithium. The α-t-butyl derivative did not undergo rearrangement when heated with acid, in contrast to 2,2-dimethyl-1,1-diphenylpropan-1-ol.[10]

Experimental

1,1-*Bis*-(p-*dimethylaminophenyl*)*butan*-1-*ol*.—Propyl-lithium, from propyl bromide (6·15 g.) in ether, was added in nitrogen to Michler's ketone (2·7 g.) in ether and after 1 hr. the mixture was poured into water. The residue from the dried (Na_2SO_4) organic layer was twice crystallised from ethanol containing a trace of sodium hydroxide, giving the *hydroxy-compound* (2·7 g.), m. p. 111—112° (Found: C, 76·6; H, 8·8; N, 8·8. $C_{20}H_{28}N_2O$ requires C, 76·8; H, 9·0; N, 8·9%).

1,1-*Bis*-(p-*dimethylaminophenyl*)*pentan*-1-*ol*.—Butyl-lithium, from butyl bromide (6·85 g.), gave, by the aforementioned method, the *hydroxy-compound* (3·0 g.), m. p. 116—117° (Found: C, 77·2; H, 9·1; N, 8·3. $C_{21}H_{30}N_2O$ requires C, 77·2; H, 9·3; N, 8·6%).

1,1-*Bis*-(p-*dimethylaminophenyl*)-3-*methylbutan*-1-*ol*.—Isobutyl-lithium, from isobutyl bromide (6·85 g.), gave, by the aforementioned method, the *hydroxy-compound* (3·0 g.), m. p. 126—127° (Found: C, 77·6; H, 9·5; N, 8·5%).

1,1,3,3,-*Tetra*-(p-*dimethylaminophenyl*)*but*-1-*ene*.—1,1-Bis-(*p*-dimethylaminophenyl)ethylene (1·0 g.) in acetic acid (20 c.c.) was kept for 48 hr. and then poured into an excess of aqueous sodium hydroxide at 0°. The crystalline precipitate, twice crystallised from ethanol, gave the *base*, m. p. 174—176° (Found: C, 80·9; H, 8·0; N, 10·0. $C_{36}H_{44}N_4$ requires C, 81·2; H, 8·3; N, 10·5%).

One of us (G. H.) thanks the Department of Scientific and Industrial Research for a grant.

The University, Hull. [*Received, October 12th*, 1960.]

[5] Kohler and Patch, *J. Amer. Chem. Soc.*, 1916, **38**, 1210.
[6] Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 152.
[7] Lemoult, *Compt. rend.*, 1911, **152**, 963.
[8] Madelung and Völker, *J. prakt. Chem.*, 1927, **115**, 40.
[9] Bartlett, Swain, and Woodward, *J. Amer. Chem. Soc.*, 1941, **63** 3229.
[10] Rogers, Brown, Rasmussan, and Heal, *J. Amer. Chem. Soc.*, 1953, **75**, 2991.

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268. *Carboxymethyldichloroarsine and Related Carboxylic Acids containing Arsenic.*

By D. Hamer and R. G. Leckey.

The reported formation of carboxymethyldichloroarsine by the action of phosphorus trichloride on carboxymethylarsonic acid, which involves the reduction of quinquevalent arsenic to the tervalent state, has been examined and confirmed. The structure, stability, and infrared spectra of the dichloroarsine are discussed and two new related acids reported.

Carboxymethyldichloroarsine (dichloroarsinoacetic acid), $Cl_2As{\cdot}CH_2{\cdot}CO_2H$, was prepared by Steinkopf and Schmidt [1] by the action of phosphorus trichloride on carboxymethylarsonic acid, $(HO)_2AsO{\cdot}CH_2{\cdot}CO_2H$. The preparation was repeated by Marquez [2] but these workers did not establish the constitution except by elemental analysis. Braunholtz and Mann [3] commented that reduction of the arsenic to the tervalent state, in preference to the formation of the chloride of the carboxylic acid, was surprising.

[1] Steinkopf and Schmidt, *Ber.*, 1928, **61**, 675.
[2] Marquez, *Rev. Fac. Cienc. quim., Univ. nac. La Plata*, 1941, **16**, 109.
[3] Braunholtz and Mann, *J.*, 1957, 3285.

We have now found that, provided the conditions are carefully controlled, the dichloroarsine can be satisfactorily prepared. The structure of the acid has been established and dibromocarboxymethylarsine and 2-carboxyethyldichloroarsine have been similarly obtained.

Carboxymethylarsonic acid was prepared by a modification of Palmer's method,[4] being separated as its barium salt. It was then converted into the dichloroarsine by phosphorus trichloride in carbon tetrachloride. The manipulative stages were critical, a feature not reported by earlier workers: with suitable precautions, reasonable yields (*ca.* 25%) were obtained. The dichloroarsine was stable when pure if moisture was excluded.

Analytical results for the dichloro-arsine were variable owing to the instability of the compound but all support a value of 205 for the molecular weight and the tervalent state of the arsenic. Direct titration with barium hydroxide gave an equivalent weight of 69·9. Non-aqueous titration with potassium methoxide gave a value of 105·5 on rapid titration but the compound slowly reacted further with the methoxide and (after back-titration with benzoic acid) an equivalent weight of 70 was obtained. Determination of the equivalent weight with iodine and with bromate gave equivalent weights of 208·2 and 204·2 for the tervalent arsenic compound. The molecular weight was also confirmed by ebullioscopic measurements in acetone and in carbon tetrachloride.

The infrared spectra examined are tabulated. The dichloroarsine has the characteristic

Compound	ν_{OH} (cm.$^{-1}$)	ν_{CO} (cm.$^{-1}$)	ν_{OH} (cm.$^{-1}$)
$Cl_2As{\cdot}CH_2{\cdot}CO_2H$ [a]	2660, 2560	1685	890
" [b]	2600, 2540	1675	885—915
$(HO)_2AsO{\cdot}CH_2{\cdot}CO_2H$ [c]	2400	1690	885
AcOH [d]	2660, 2570	1712 ± 5	930
$Cl{\cdot}CH_2{\cdot}CO_2H$ [d]	2700, 2590, 2540	1713	933
$Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ [d]	2640, 2580	1715	910
$Ph{\cdot}AsCl{\cdot}CH_2{\cdot}CO_2H$ [3]	2640, 2540	1683	945, 920

[a] Hexachlorobutadiene mull. [b] KBr disc. [c] Nujol mull. [d] Flett, *J.*, 1951, 962.

O–H and C=O bands associated with carboxylic acids though the inductive effect of the arsenic and chlorine atoms influences the position of the maxima. The existence of hydrogen bonding often encountered in structures such as carboxylic acids, which are capable of dimerisation, was demonstrated. The strong vibrational C–O band in the region 1770—1815 cm.$^{-1}$, usually present in the spectra of acid halides, was absent.

It is not possible to offer any evidence to support any particular path for the reduction of the quinquevalent arsenic in the arsonic acid into the tervalent state by the phosphorus trichloride. Consideration of the following reaction scheme, using available bond-energy data,[5] suggests that the reactions could take place and that reaction (i) would indeed be exothermic.

(i) $H_2O_3As{\cdot}CH_2{\cdot}CO_2H + PCl_3 \longrightarrow POCl_3 + (HO)_2As{\cdot}CH_2{\cdot}CO_2H$

(ii) $(HO)_2As{\cdot}CH_2{\cdot}CO_2H \xrightarrow[POCl_3]{PCl_3 \text{ or}} HO{\cdot}AsCl{\cdot}CH_2{\cdot}CO_2H \longrightarrow Cl_2As{\cdot}CH_2{\cdot}CO_2H$

By essentially the same method two new acids, dibromocarboxymethylarsine and 2-carboxyethyldichloroarsine were prepared, the former less stable than the corresponding dichloro-acid. The new acid where the arsenic atom was separated from the carboxyl group by two methylene units was more stable, in accord with Braunholtz and Mann's observations [3] on the stabilities of di-(2-carboxyethyl)phenylarsine and related compounds. Attempts to isolate pure 1-carboxyethyldichloroarsine were unsuccessful; the product seemed very unstable, though this may have been due to impurities.

Experimental

Carboxymethylarsonic Acid.—The following modification of Palmer's method [4] was used. Arsenic trioxide (99 g.) and sodium hydroxide (160 g.) were dissolved in water (300 ml.), and

[4] Palmer, *J. Amer. Chem. Soc.*, 1923, **45**, 3023.
[5] Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 2nd edn., 1958.

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the solution was cooled to 30°. Monochloroacetic acid (47·3 g.) was added and the mixture stirred for 2 hr. The solution was then carefully neutralised with glacial acetic acid, the addition of acid being controlled potentiometrically. The mixture was set aside for 12 hr. at 20°, filtered, and added to aqueous barium chloride (185 g. in 500 ml.). The barium salt was washed, dried at 130° (yield 185 g., 83%), and decomposed at room temperature by addition of 10% less than the equivalent of 2N-sulphuric acid. The arsonic acid was isolated from the aqueous solution by lyophilising, as solutions of the free acid decomposed readily when warmed. It recrystallised from glacial acetic acid (yield 55 g., 74%) and had m. p. 152° (Found: As, 40·65. Calc. for $C_2H_5AsO_5$: As, 40·7%).

2-Carboxyethylarsonic acid, made from β-chloropropionic acid by the same method, had m. p. 146° (Found: As, 37·95. Calc. for $C_3H_7O_5As$: As, 37·85%).

Carboxymethyldichloroarsine.—This compound was prepared by the route used by Steinkopf and Schmidt [1] but all operations were carried out under nitrogen. Reactants and solvents were freshly dried and distilled. Carboxymethylarsonic acid (15 g.) was suspended in carbon tetrachloride (25 ml.) and to this was added slowly phosphorus trichloride (35 g.) in the same solvent (50 ml.). The reaction is exothermic and the vessel must be kept below 30°. After 1½ hr. the mixture was cooled to −5°, and the product washed with cold carbon tetrachloride and then extracted in ether. This extract was evaporated at once and the acid recrystallised from carbon tetrachloride. Finally the white crystalline product was dried under reduced pressure at 56°. The yield was 4·5 g. (27%), and the m. p. 122° (Found: As, 36·2; Cl, 34·7. Calc. for $C_2H_3AsCl_2O_3$: As, 36·6; Cl, 34·6%).

Dibromocarboxymethylarsine.—This method was similar to that used for the dichloro-compound, with phosphorus tribromide (69 g.) instead of the trichloride. Reaction was rapid and exothermic and it was important to keep the temperature at 15°. At higher temperatures the product decomposed to a brown oil. Rapid recrystallisation was also necessary, otherwise the white crystals decomposed. However, once the acid was dry and free from phosphorus contaminants it seemed stable. The yield of crystalline *dibromocarboxymethylarsine*, m. p. 108—112°, was 4 g. (24%) (Found: As, 24·4; Br, 53·3. $C_2H_3AsBr_2O_3$ requires As, 25·5; Br, 54·4%).

2-Carboxyethyldichloroarsine.—2-Carboxyethylarsonic acid (16 g.) was suspended in carbon tetrachloride (25 ml.), and phosphorus trichloride (35 g.) in the same solvent (50 ml.) was added, after initial cooling in a freezing mixture. Vigorous stirring was necessary and the temperature had to be kept below 15°. The *acid* was extracted and purified as before. After a second recrystallisation from carbon tetrachloride, it had m. p. 90° (2 g., 12%) (Found: As, 34·1; Cl, 32·4. $C_3H_5AsCl_2O_3$ requires As, 34·2; Cl, 32·4%).

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NOTES.

269. *Derivatives of Fluorene. Part XII.* 2-Amino-9-bromofluorene Hydrobromide and Related Compounds.*

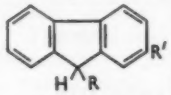
By T. Lloyd Fletcher and Moses J. Namkung.

With a view to synthesis of potential drugs and continuing previous work we have obtained 2-amino- and 2-acetamido-9-bromofluorene (I; R = Br, R′ = NH_2 and NHAc respectively) in good yield by heating the corresponding 9-hydroxy-compounds [1] with 48% hydrobromic acid in acetic acid at 100° for a short time; more drastic conditions were needed to provide 9-bromo-2-dimethylaminofluorene. Dickinson and Eaborn [2] failed to convert 2-aminofluorene into the bromo-compound by *N*-bromosuccinimide, and this method failed in our hands for the acetyl derivative.

* Part XI, *J. Org. Chem.*, 1960, **25**, 1348.

[1] Pan and Fletcher, *J. Org. Chem.*, 1958, **23**, 799.
[2] Dickinson and Eaborn, *J.*, 1959, 2337.

Base converts 2-amino-9-bromofluorene into an insoluble high-melting product, presumably a bi-9-fluorenylidene derivative.



(I)

The 9-bromine atom was replaced without difficulty by reaction with pyrrolidine, morpholine, or piperidine to give the 9-substituted derivatives; and reaction with ethyl sodioacetamidomalonate gave compounds (I) in which R = $C(NHAc)(CO_2Et)_2$.

Some standard derivatives of the products have been prepared. Absorption spectra are tabulated.

Experimental.—M. p.s are corrected.

2-Amino-9-bromofluorene hydrobromide. 2-Aminofluoren-9-ol (50 g., 0·255 mole) was heated in acetic acid (300 ml.) and 48% hydrobromic acid (100 ml., 0·9 mole) on a steam-bath for 30 min., during which a precipitate was formed. After cooling, this *salt* was removed and dried (83 g., 95·5%); it crystallised from acetic acid (Found: C, 46·0; H, 3·4; N, 4·2; Br, 47·1. $C_{13}H_{10}BrN,HBr$ requires C, 45·8; H, 3·3; N, 4·1; Br, 46·9%).

2-Acetamido-9-bromofluorene, m. p. 213—214° (from alcohol) (Found: C, 59·5; H, 4·2; N, 4·75. $C_{15}H_{12}BrNO$ requires C, 59·6; H, 4·0; N, 4·6%), was obtained similarly in 56·5% yield and (96% yield) by treating the amine hydrobromide with acetic anhydride on a steam-bath for 30 min.

9-Bromo-2-NN-dimethylaminofluorene hydrobromide. When 2-*NN*-dimethylaminofluoren-9-ol (10 g.) was heated at 60° with 48% hydrobromic acid (10 ml.) in acetic acid (60 ml.) for 30 min. no precipitate was obtained even after cooling. The solution was concentrated to 15 ml., a further 5 ml. of 48% hydrobromic acid were added, and the whole was set aside. Crystals which were then deposited were filtered off, washed with acetic acid (10 ml.), and dried (P_2O_5; NaOH; 1 mm.) (yield 97%). This *hydrobromide* crystallised from acetic acid (Found: C, 48·7; H, 4·2; N, 3·7; Br, 42·9. $C_{15}H_{14}BrN,HBr$ requires C, 48·8; N, 4·1; N, 3·8; Br, 43·3%).

2-Acetamido-9-morpholinofluorene. Morpholine (3·5 g.) was added dropwise to a solution of 2-acetamido-9-bromofluorene (6·04 g.) in boiling ethanol (300 ml.), the whole concentrated to 50 ml. and cooled, and the product (5·2 g., 84%) filtered off, dried, and recrystallised from methanol (charcoal); it had m. p. 234—236° alone or mixed with an authentic sample.[3]

Similarly were prepared *2-acetamido-9-piperidinofluorene* (93·5% yield), m. p. 204—205° (from methanol) (Found: C, 78·1; H, 7·0; N, 9·3. $C_{20}H_{22}N_2O$ requires C, 78·4; H, 7·2; N, 9·1%), and *2-acetamido-9-pyrrolidinofluorene* (100% yield), m. p. 211—212° (from methanol) (Found: C, 77·8; H, 6·9; N, 9·4. $C_{19}H_{20}N_2O$ requires C, 78·0; H, 6·9; N, 9·6%).

2-Amino-9-piperidinofluorene. 2-Amino-9-bromofluorene hydrobromide afforded 9-bromo-2-trifluoroacetamidofluorene, m. p. 180—182° alone or mixed with an authentic sample.[3] To this compound (0·89 g.) in ethanol (20 ml.) was added dropwise piperidine (0·64 g., 3 equiv.), and the mixture was boiled for 10 min. Then 2N-sodium hydroxide was added to turbidity and the whole poured into water (100 ml.). The precipitated *diamine* (100% yield) was collected and twice recrystallised from ethanol, then having m. p. 173—173·5° (Found: C, 81·7; H, 7·3; N, 11·0. $C_{18}H_{20}N_2$ requires C, 81·8; H, 7·6; N, 10·6%).

2-Arylideneamino-9-morpholinofluorenes. Equimolar amounts of 2-amino-9-morpholinofluorene and benzaldehyde were heated in a small amount of ethanol for 1 hr. and then set aside. The precipitated *2-benzylideneamino-compound* recrystallised from methanol in needles, m. p. 156—157° (Found: C, 81·0; H, 6·0; N, 7·9. $C_{24}H_{22}N_2O$ requires C, 81·3; H, 6·2; N, 7·9%).

After a similar reaction with *p*-dimethylaminobenzaldehyde, the mixture was poured into water and made alkaline with aqueous ammonia. The precipitated gummy *2-p-dimethylaminobenzylideneamino-compound* solidified and, recrystallised from benzene (charcoal), had m. p. 238·5—239·5° (yield, two crops, 96%) (Found: C, 78·55; H, 7·0; N, 10·3. $C_{26}H_{27}N_3O$ requires C, 78·6; H, 6·8; N, 10·6%).

Diethyl α-acetamido-α-(2-acetamido-9-fluorenyl)malonate. 2-Acetamido-9-bromofluorene (6·04 g.) in absolute ethanol (100 ml.) was added slowly to a boiling solution of diethyl acetamidomalonate (4·34 g.) and sodium (0·46 g.) in absolute ethanol (200 ml.). The mixture was concentrated to 50 ml. and cooled, and the precipitate filtered off, washed with water (to remove sodium bromide), dried (yield, 6·9 g., 79%), and crystallised from ethanol. This ester had m. p. 197—198° alone or mixed with the compound described below.

[3] Fletcher and Namkung, *J. Org. Chem.*, 1958, **23**, 680.

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Absorption spectra of fluorene derivatives (I).

Substituents [a]		Ultraviolet			Infrared (mμ)		
R	R′	Concn.[b] (10^{-5}M)	$\lambda_{max.}$ [c] (mμ)	log ε	Amide N–H	Amide C=O	Others
$C_5H_{10}N$ [d]	H	3·33	307, 295, 268, 262, 230, 222	3·67, 3·79, 4·28, 4·28, 4·07, 4·31			
C_4H_8NO [e]	H	3·33	307, 295, 261, 230, 223	3·61, 3·50, 4·20, 4·22, 4·44			C–O–C 1113
C_5H_9N	NH_2	3·33	298	4·34			
$C_5H_{10}N$	NH_2	3·33	298	4·31			
C_4H_8NO	NH_2	3·33	297	4·37			C–O–C 1110
X	NH_2	3·33	297	4·33	1630	1670	Acid C=O 1760, 1730
C_4H_8N	NHAc	3·33	*307*, 294, *286*	4·22, 4·38, 4·33	1600	1660	
$C_5H_{10}N$	NHAc	3·33	*307*, 294, *286*	4·24, 4·39, 4·34	1600	1660	
C_4H_8NO	NHAc	3·33	*307*, 294, *284*	4·25, 4·40, 4·33	1600	1660	C–O–C 1115
X	NHAc	3·33	*305*, 293	4·33, 4·45	{1600 1620	1665 1710	Acid C=O 1760, 1740
C_4H_8NO	NH·CO·CF_3	3·33	*310*, 295	4·27, 4·40	1620	1730	C–O–C 1110, CF_3 1200
Br	NHAc	2·5	307, 297, 252	4·37, 4·40, 4·41	1620	1680	
Br	NH·CO·CF_3	2·5	298, 252	4·25, 4·24	1620	1710	CF_3 1200
X	NO_2	3·33	330, 280	4·25, 4·17	1620	1670	Acid C=O, 1760, 1740; Aryl NO_2 1340, 1525
Br	NH_2,HBr	2·0	308, 247	4·15, 4·36			[g] N^{IV} 3050—2800sbr, 2555, 1920, 1610, 1350, 830
		3·33	*275*, 246	4·33, 4·46			
Br	NMe_2,HBr	2·0	318, 222	4·32, 4·37			[g] N^{IV} 2500, 2440, 1720
		3·33	318, *297—262*,[h] 222	4·30, 4·23 4·37			
X	H	1·0	303, *291*, *278*, 268, 232, *224*	3·59, 3·70, 4·18, 4·30, 4·13, 4·37	1625	1650	Acid C=O 1760, 1745
		2·0	303, *291*, *278*, 268, 232, *223*	3·42, 3·57, 4·12 4·24, 4·03, 4·29			
		2·25	303, *291*, *278*, 268, *253*, 232, *223*	3·63, 3·82, 4·25, 4·35, 4·14, 4·07, 4·31			
		2·5	268, 232	4·64, 4·14			
H	NH_2,HCl	—	—	—			[g] N^{IV} 3050—2750sbr, 2550, 1980, 1600, 1350, 812
C_4H_8NO	NH:CHPh	—	—	—			C–O–C 1113, C=N 1630
C_4H_8NO	NH:CH·C_6H_4·NMe_2-*p*	—	—	—			C–O–C 1113, C=N 1640, Aryl NMe_2 1370, 1235

[a] $C_5H_{10}N$ = piperidino, C_4H_8N = pyrrolidino, C_4H_8NO = morpholino, X = $C(NHAc)(CO_2Et)_2$. [b] In absolute EtOH. [c] Italicised values are for shoulders. [d] Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 377. [e] Bamford and Stevens, *J.*, 1952, 4675. [f] After 24 hr. absorption had increased at shorter wavelengths. [g] Jones ("Infrared Spectra of Organic Compounds: Summary Chart of Principal Group Frequencies," N.R.C. Bull. No. 6, 1959, Ottawa, Canada) gives for bonded N–H stretching in quaternary amine salts complex bands at 2900—2300 cm.$^{-1}$; Colthup (*J. Opt. Soc. Amer.*, 1950, **40**, 397) gives for amine hydrochloride 2500—2780 cm.$^{-1}$; Bellamy ("Infrared Spectra of Complex Molecules," J. Wiley and Sons Co. Inc., New York, 2nd edn., 1958, p. 259) gives NH_2 deformn. frequency near 1600 cm.$^{-1}$, symmetric mode near 1300 cm.$^{-1}$, NH_3 rocking frequency near 800 cm.$^{-1}$, and (p. 260) NH^+ 2200—1800 cm.$^{-1}$.

Diethyl α-acetamido-α-9-fluorenylmalonate * *and compounds derived from it.* After addition of 9-bromofluorene (122·5 g.) in ethanol (500 ml.) to a boiling solution of diethyl α-acetamidomalonate (108·5 g.) and sodium (11·5 g.) in absolute ethanol (600 ml.), the mixture was concentrated to 1 l. and cooled, precipitated sodium bromide was removed, and the filtrate concentrated to 300 ml. and left to cool. The precipitated *ester* (73 g., 39%) was collected; a further 67 g. (35%) were obtained by further concentration of the filtrate. Crystallisation from toluene gave material of m. p. 127—128° (Found: C, 69·4; H, 6·1; N, 3·5. $C_{22}H_{23}NO_5$ requires C, 69·3; H, 6·1; N, 3·7%).

* The authors thank Mr. W. H. Wetzel for some assistance in this and the following experiment.

Adding nitric acid (*d* 1·42; 76 ml.) and concentrated sulphuric acid (15 ml.) to the foregoing ester (76°, 2 g.) in acetic acid at 50° and later heating at 65° gave, by the usual working up, *diethyl α-acetamido-α-(2-nitro-9-fluorenyl)malonate* (67 g.), m. p. 183·5—184° (from ethanol) (Found: C, 61·7; H, 5·3; N, 6·6. $C_{22}H_{22}N_2O_7$ requires C, 61·9; H, 5·2; N, 6·6%).

The nitro-ester (42·6 g.) was reduced by hydrazine hydrate (25 ml.) and Raney nickel in ethanol (2·5 l.) (cf. ref. 3) to the *2-aminofluorenyl ester* (95·5%), m. p. 173—174° (from ethyl acetate) (Found: C, 66·9; H, 5·9; N, 7·5. $C_{22}H_{24}N_2O_5$ requires C, 66·65; H, 6·1; N, 7·1%). With acetic anhydride at 100° in 5 min. this gave the above-mentioned *2-acetamidofluorenyl ester*, m. p. 197—198° (Found: C, 65·5; H, 6·1; N, 6·7. $C_{24}H_{26}N_2O_6$ requires C, 65·7; H, 6·0; N, 6·4%).

The nitro-ester (1 g.), when boiled with sodium dichromate (10 g.) in glacial acetic acid (100 ml.) for 1 hr., gave 2-nitrofluorenone (95%), m. p. and mixed m. p. 224—224·5°.

We thank the National Cancer Institute, National Institutes of Health, U.S.P.H.S., for aiding this work, in part, with a grant (CY-1744). Microanalyses were done by Alfred Bernhardt, Microanalytical Laboratories, Mülheim (Ruhr), and by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Ultraviolet spectra were obtained on a Beckman DK-1 recording instrument. Infrared spectra were for potassium bromide discs, measured on a Beckman IR-5 instrument. We are grateful to Barbara J. Bigley and Karen Olsoe for technical assistance.

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270. *The Pyrolysis of* 1,3,5-*Trioxan.*

By W. Hogg, D. M. McKinnon, A. F. Trotman-Dickenson, and G. J. O. Verbeke.

Burnett and Bell [1] found that the gas-phase thermal decomposition of 1,3,5-trioxan between 272° and 347° is a homogeneous unimolecular reaction whose rate constant at pressures above 15 mm. is given by $\log k\ (\text{sec.}^{-1}) = 14{\cdot}8 - (47{,}400/2{\cdot}3RT)$. At 312° the rate constant falls rapidly as the pressure is reduced to 0·1 mm. The reaction, therefore, appeared to be suitable for a test of theories of unimolecular reaction. It does not involve free radicals and occurs at comparatively low temperatures so that the effect of many inert gases could be studied.

We have re-investigated the reaction at 272°, 312°, and 347°. The first-order plots were linear for four half-lives and the final pressure was always close to three times the initial pressure, as required by the equation, $(CH_2O)_3 = 3CH_2O$. The rate constant with 20—80 mm. initial pressure was given by (22 runs) $\log k\ (\text{sec.}^{-1}) = 14{\cdot}95 - (47{,}400/2{\cdot}3RT)$. Several runs were done at each of the temperatures with 5—90 mm. pressure after the reaction vessel had been packed with Pyrex tubes so as to increase the surface:volume ratio 3·3 times. The mean points were very slightly lower than those given by the Arrhenius equation, but by little more than the normal scatter. There is no evidence for a fast heterogeneous reaction. Burnett and Bell had difficulty in preparing and drying their trioxan. Frequently their final pressures were much less than three times the initial pressures. The present results are, therefore, to be preferred.

The decomposition was followed at initial pressures down to 0·1 mm. (340° and 312°) and 0·5 mm. (272°). At 340° the rate fell to one-quarter of its high-pressure value, with no sign of breaks in the plots of $\log k$ against $\log p$. The decline was much less marked at low temperatures. The A factors and activation energies at the various pressures are:

Pressure (mm.)	0·1	1	10	100
$\log A$ (sec.^{-1})	11·0	12·3	14·5	15·0
E (kcal. mole^{-1})	35·6	39·5	45·8	47·4

Theories of unimolecular reaction predict such variations of Arrhenius parameters with pressure, but the observed values vary too sharply to be explained on these lines. Possibly heterogeneous processes are important at the lowest pressures and temperatures.

The variation of rate constant with pressure at 312° is compared below with that

[1] Burnett and Bell, *Trans. Faraday Soc.*, 1938, **34**, 420.

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observed by Burnett and Bell, whose determinations were rather more scattered. The present curve is less convex by an amount that is probably outside experimental error.

log p (mm.)	2	1·5	1·0	0·5	0	−0·5	−1·0
log k/k: present work	0·00	−0·02	−0·08	−0·18	−0·28	−0·36	−0·47
Burnett and Bell	0·00	−0·02	−0·07	−0·12	−0·21	−0·34	−0·52

Experimental.—1,3,5-Trioxan (Eastman) was degassed and purified by bulb-to-bulb sublimation at low pressure with rejection of considerable end fractions. Different samples gave identical rate constants.

Two apparatus, to which several of the components were common, gave identical results. The second version had a Pyrex reaction vessel (385 c.c.) contained in a mercury-vapour jacket. The outer jacket was wound with heating-tape and lagged. The vessel was inclined to the horizontal so that mercury that entered accidentally from the manometers ran out again. A precise temperature was maintained in the vessel by adjustment of the pressure of the mercury-boiler. The reaction vessel was attached by 1·5 mm. capillary to the storage vessel, the vacuum-line, and three manometers. The first manometer had one arm of 2 cm. diameter and the other a 2 mm. capillary tube. The second was a butyl phthalate–mercury manometer that gave a magnification of 8·9. The third was a McLeod gauge, of 10·7 c.c. total capacity, giving multiplication factors of 24, 92, and 500 when used with a linear scale. All the taps (silicone grease), the tubing, and the McLeod were wound with electric heating-tape and kept slightly above 100°.

Thanks are offered for an Imperial Chemical Industries Fellowship held by G. J. O. V.

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271. *Polycyclic Cinnoline Derivatives. Part VII.*[1] *Benzo*[c][^{15}N]*cinnoline.*

By P. F. HOLT, B. I. HOPSON-HILL, and C. J. MCNAE.

IN the study of the nitration of benzo[*c*]cinnoline, quantitative isolation of the nitro-derivatives, which is difficult, can be obviated by the method of isotopic dilution making use of nitrobenzo[*c*][^{15}N]cinnolines. A method has therefore been sought for the preparation of ^{15}N-labelled benzo[*c*]cinnoline in good yield. Benzo[*c*]cinnolines are usually prepared by reducing 2,2′-dinitrobiaryls, which are obtained from *o*-halogeno-nitroaryls by the Ullmann reaction. To this end *o*-bromo[^{15}N]nitrobenzene has been prepared,[2] but only in poor yield.

The several methods which have been described for converting biphenylbisdiazonium salts into benzo[*c*]cinnolines, by forming a diaza-link and eliminating nitrogen, offer the possibility of the introduction of nitrogen-15 from labelled nitrite, provided that the elementary nitrogen produced in the reaction is not derived solely from the external nitrogen atoms. Three of these reactions have been examined.

(*a*) Täuber[3] formed benzo[*c*]cinnoline by reducing biphenyl-2,2′-bisdiazonium salts and heating the resulting dihydrazino-compound with hydrochloric acid at 150°. The benzo[*c*]cinnoline formed from 2,2′-di[β-^{15}N]hydrazinobiphenyl dihydrochloride by this method retained only a part of the nitrogen-15, indicating that mechanisms involving both N–N and C–N fission, but mainly the former, were involved. An assay of the ^{15}N abundance in the ammonia formed in the reaction confirmed this result. As a method for the production or labelled benzo[*c*]cinnoline, it is not efficient enough for our purpose.

(*b*) Dobbie, Fox, and Gauge[4] reported that benzo[*c*]cinnoline together with carbazole was formed from biphenyl-2,2′-bisdiazonium bromide by the action of cuprous bromide, instead of the expected 2,2′-dibromobiphenyl. Mechanisms for this reaction have been suggested.[5,6] Following the procedure of Dobbie, Fox, and Gauge, we have been unable

[1] Part VI, *J.*, 1861, 1363.
[2] McNae, unpublished result.
[3] Täuber, *Ber.*, 1896, **29**, 2270.
[4] Dobbie, Fox, and Gauge, *J.*, 1911, **99**, 1615.
[5] Saunders and Waters, *J.*, 1946, 1154; Hodgson, *J.*, 1948, 348.
[6] Saunders, "The Aromatic Diazo Compounds," Arnold, London, 1949, p. 263.

to produce either carbazole or benzo[*c*]cinnoline but have obtained 2,2′-dibromobiphenyl.

(*c*) Sandin and Cairns [7] showed that, while diazonium salts normally give arylarsonic acids with sodium arsenite, diazotised 2,2′-diaminobiphenyl gives benzo[*c*]cinnoline. Two mechanisms have been suggested for this reaction,[5] both of which involve the initial elimination of one diazonium group and the formation of the pyridazine ring from the other. Biphenyl-2,2′-bisdiazonium chloride, prepared by diazotising the amine with [^{15}N]nitrite, was decomposed with arsenite to give a cinnoline which retained half the nitrogen-15 of the nitrite. The result would be expected from either of the proposed mechanisms. This appears to be a satisfactory method of preparing benzo[*c*]cinnoline.

It is not known how far this reaction is applicable to the preparation of other labelled cinnolines. Sandin and Cairns also converted 2,2′-diamino-4,4′-dimethylbiphenyl into the corresponding cinnoline derivative and concluded that the reaction was general, but we have found it does not occur with 2-*o*-diazoniophenylnaphthalene-1-diazonium chloride.

Experimental.—Potassium [^{15}N]*nitrite.* Potassium [^{15}N]nitrite was prepared from potassium [^{15}N]nitrate by the method previously described [8] or, in better yield, by Heath's method [9] using lead powder.

2,2′-Diaminobiphenyl. 2,2′-Dinitrobiphenyl (3·0 g.) on catalytic reduction [10] yielded the diamine (2·0 g.; m. p. 79°; lit., 80°); alternatively, reduction by the method of More and Furst [11] yielded 1·71 g. of diamine (m. p. 77—78°) from 2·44 g.

2,2′-Di[β-^{15}N]*hydrazinobiphenyl dihydrochloride.* Täuber's method [3] was repeated, with potassium [^{15}N]nitrite, to obtain the dihydrazine from 2,2′-diaminobiphenyl (1·32 g.). The product was contaminated with sodium chloride.

To characterise the compound, a small sample of 2,2′-di[^{15}N]hydrazinobiphenyl was prepared by shaking the dihydrochloride with an excess of ammonia and extracting the solution with benzene. The concentrated solution gave orange-brown crystals, m. p. 103—105° (Täuber [3] gives 110°).

Benzo[c]*cinnoline from 2,2′-di*[β^{15}N]*hydrazinobiphenyl dihydrochloride.* The dihydrazino-compound, sealed in a tube with 20% hydrochloric acid (6 ml.), was kept at 160° ± 7° for 3 hr. (cf. Täuber,[3] 150°, 1 hr.) and the product precipitated in aqueous sodium carbonate. Micro-sublimation gave benzo[*c*]cinnoline, m. p. 152—153° (lit., 156°).

Benzo[c][^{15}N]*cinnoline.* 2,2′-Diaminobiphenyl (0·50 g.) was converted by Sandin and Cairns' method [7] using potassium [^{15}N]nitrite (atom % ^{15}N 32·4) into *benzo*[c][^{15}N]*cinnoline*, (0·12 g.; m. p. 154—156°). The [^{15}N]-abundance of the bisdiazonium compound was assumed to be half that of the potassium nitrite. For results see the Table.

Compound decomposed	Atom % of ^{15}N	Benzo[*c*]-cinnoline, atom % of ^{15}N	Ammonia, atom % of ^{15}N	For N–N break	For C–N break
2,2′-Dihydrazinobiphenyl.....	17·1	6·2	—	0·37	17·1
	16·4	3·9	—	0·37	16·4
		—	27·0	32·8	0·37
Biphenyl-2,2′-bisdiazonium chloride	16·2	15·8	—	0·37	16·2

Atmospheric abundance, atom % of ^{15}N: 0·37

Two of us (B. I. H-H. and C. J. M.) acknowledge grants from the Department of Scientific and Industrial Research.

THE UNIVERSITY, READING. [*Received, August 3rd,* 1960.]

[7] Sandin and Cairns, *J. Amer. Chem. Soc.*, 1936, **58**, 2019.
[8] Holt and Hopson-Hill, *J.*, 1952, 4251.
[9] Heath, *J.*, 1957, 4152.
[10] Adams, Cohen, and Rees, *J. Amer. Chem. Soc.*, 1927, **49**, 1093.
[11] More and Furst, *J. Org. Chem.*, 1958, **23**, 1504.

272. *The Reduction of Diaryl Ketones and Diarylmethanols to Diarylmethanes.*

By J. BLACKWELL and W. J. HICKINBOTTOM.

A LARGE number of nuclear substituted diphenylmethanes were required for another investigation. It was found that they could be prepared most conveniently by reduction

TABLE 1. *Diphenylmethanes prepared from substituted benzophenones.*

Subst.	B. p./mm.	n_D^{20}	Yield (%)	Found (%) C	Found (%) H	Found (%) Hal.	Formula	Required (%) C	Required (%) H	Required (%) Hal
2-Cl	157°/10 [a]	1·5889	89							
3-Cl	161°/12	1·5867	90	77·0	5·7	17·1	$C_{13}H_{11}Cl$	77·0	5·5	17·5
4-Cl	160°/11 [a]	1·5854	90	—	—	—		—	—	—
2-Br	166—167°/16 [b]	1·6100	91	—	—	—		—	—	—
3-Br	129—130°/1·0	1·6056	90	62·8	4·6	32·8	$C_{13}H_{11}Br$	63·1	4·5	32·4
4-Br	164°/14 [a]	1·6045	90	—	—	—		—	—	—
2-I	177°/12 [d]	1·6406	90	—	—	—		—	—	—
3-I	181°/12	1·6389	89	53·2	3·8	43·3	$C_{13}H_{11}I$	53·1	3·7	43·2
4-I *	M. p. 43—44° [e]	—	88	—	—	—		—	—	—
2-F	74°/0·2	1·5586	90	83·6	5·9	10·2	$C_{13}H_{11}F$	83·8	6·0	10·2
3-F	75°/0·2	1·5563	90	83·5	5·9	10·5	$C_{13}H_{11}F$	83·8	6·0	10·2
4′-Cl-3-OMe	198—199°/17	1·5798	88	72·0	5·8	15·4	$C_{14}H_{13}ClO$	72·2	5·6	15·3
2-Br-4′-Cl	129°/0·4	1·6138	90	55·1	3·8	28·1 [f]	$C_{13}H_{10}BrCl$	55·4	3·6	28·4 [f]
3-Br-4′-Cl	132—133°/0·5	1·6117	90	55·1	3·8	28·4 [g]	$C_{13}H_{10}BrCl$	55·4	3·6	28·4 [g]
4-Cl-2′-I	151—152°/0·3	1·6440	88	47·5	3·2	10·5	$C_{13}H_{10}ClI$	47·5	3·1	10·8
4-Cl-3′-I	150°/0·2	1·6428	89	47·7	3·0	11·0	$C_{13}H_{10}ClI$	47·5	3·1	10·8
4-Cl-4′-I	148°/0·2	m. p. 47°	89	47·8	3·3	10·5	$C_{13}H_{10}ClI$	47·5	3·1	10·8
4-Cl-2′-F	91—92°/0·2	1·5680	90	70·5	4·7	16·1 [h]	$C_{13}H_{10}ClF$	70·7	4·6	16·1 [h]

* Added by Soxhlet extraction. [a] Cf. Tschitschibabin and Schlesser, *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 151. [b] Cf. Bergmann, *J. Org. Chem.*, 1939, **4**, 1. [c] Cf. Speer and Hill, *J. Org. Chem.*, 1937, **2**, 139. [d] Cf. Seidel, *Ber.*, 1928, **61**, 2276. [e] Cf. Akagi and Iwashige, *J. Pharm. Soc. Japan*, 1954, **74**, 610. [f] Br (Found: Cl, 12·8. Reqd.: Cl, 12·6%). [g] Br (Found: Cl, 12·6. Reqd.: Cl, 12·6%). [h] Cl (Found: F, 8·6. Reqd.: F, 8·6%).

TABLE 2. *Diphenylmethanes prepared from substituted diarylmethanols.*

Subst.	B. p./mm.	n_D^{20}	Yield (%)	Found (%) C	Found (%) H	Found (%) Hal	Formula	Required (%) C	Required (%) H	Required (%) Hal
2-Me	141°/13 [i]	1·5762 [j]	90	—	—	—		—	—	—
3-Me	139—140°/11	1·5713 [j]	90	—	—	—		—	—	—
4-Me	140°/11 [k]	1·5692 [j]	89	—	—	—		—	—	—
2-OMe †	162°/11 [l,m,i]	—	90	—	—	—		—	—	—
3-OMe	165°/13	1·5763	91	84·9	7·2		$C_{14}H_{14}O$	84·8	7·1	
4-OMe	166°/13 [n]	1·5758 [o]	90	—	—	—		—	—	—
3-OH †	183—184°/11 [n]	—	88	84·8	6·7		$C_{13}H_{12}O$	84·7	6·6	
4-F	132°/14 [p]	1·5552	90	—	—	—		—	—	—
4′-Cl-2-Me	172—173°/11	1·5842	90	77·3	6·0	16·7	$C_{14}H_{13}Cl$	77·6	6·0	16·4
4′-Cl-3-Me	169—170°/10	1·5790	89	77·8	5·8	16·3	$C_{14}H_{13}Cl$	77·6	6·0	16·4
4′-Cl-4-Me	166—167°/9 [q]	1·5840	90	77·3	6·1	16·7	$C_{14}H_{13}Cl$	77·6	6·0	16·4
4′-Cl-2-OMe	115°/0·2 [r]	1·5840 [m]	88	72·4	5·6	15·0	$C_{14}H_{13}ClO$	72·2	5·6	15·3
4′-Cl-4-OMe	191°/14 [s]	1·5827	89	—	—	—		—	—	—
2,4′-Cl_2	185°/11 [q]	1·5976	90	—	—	—		—	—	—
3,4′-Cl_2	181°/10	1·5954	89	65·5	4·3	30·3	$C_{13}H_{10}Cl_2$	65·8	4·3	29·9
4,4′-Cl_2	M. p. 56° [r]	—	88	—	—	—		—	—	—
4-Br-4′-Cl	M. p. 52°	—	88	55·2	3·8	28·4 [x]	$C_{13}H_{10}BrCl$	55·4	3·6	28·4
4′-Cl-3-F	184—185°/30	1·5669	89	70·4	4·7	16·3 [y]	$C_{13}H_{10}ClF$	70·7	4·6	16·1
4-Cl-4′-F	159°/12	1·5663	89	71·0	4·7	15·7 [z]	$C_{13}H_{10}ClF$	70·7	4·6	16·1

† Added by Soxhlet extraction. [i] Mascarelli and Pirona, *Chem. Abs.*, 1939, **33**, 9314. [j] Lamneck and Wise, *J. Amer. Chem. Soc.*, 1954, **76**, 1104. [k] von Auwers and Frühling, *Annalen*, 1921, **422**, 224. [l] Claisen, *Annalen*, 1925, **442**, 239. [m] Stoermer and Frick, *Ber.*, 1924, **57**, 27. [n] Späth, *Monatsh.*, 1913, **34**, 2007. [o] Pratt, Preston, and Draper, *J. Amer. Chem. Soc.*, 1950, **72**, 1367. [p] Lichtenberger and Thermet, *Bull. Soc. chim. France*, 1951, 318. [q] Cristol and Haller, *J. Amer. Chem. Soc.*, 1945, **67**, 2222. [r] Stephen, Short, and Gladding, *J.*, 1920, **117**, 522. [s] M. p. 26—27°. [t] M. p. 30—31°. [u] M. p. 55°. [x] M. p. 24—25°. [y] At 25°. [z] Br (Found: Cl, 12·6. Reqd.: Cl, 12·6%). [y] Cl (Found: F, 9·0. Reqd.: F, 8·6). [z] Cl (Found: F, 8·6. Reqd.: F, 8·6%).

of the corresponding diaryl ketones and diarylmethanols by lithium aluminium hydride and aluminium chloride.[1] In this Note, the preparation of 37 diarylmethanes is reported in yields of about 90%. The method thus appears to be of fairly general application; it also has the advantage of being both convenient and rapid.

Experimental.—The following modification of Brown and White's method [1] was suitable and convenient.

Aluminium chloride (0·35 mole, 46·7 g.) in ether (100 c.c.) was added to a suspension of lithium aluminium hydride (0·175 mole, 6·6 g.) in ether (10 c.c.). The substituted benzophenone or alcohol (0·10 mole) in ether was added during 10 min., and the mixture then heated under reflux for 30 min. Excess of the reagent was destroyed by adding ethyl acetate, and the mixture was poured into 20% aqueous sulphuric acid. The ether solution, after washing and drying, was evaporated, and the product isolated by any convenient method. It was necessary in some few reductions to introduce the ketone or alcohol into the reducing medium by extraction from a Soxhlet thimble. The Tables summarise our results.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1. [*Received, August 3rd*, 1960.]

[1] Brown and White, *J.*, 1957, 3755; Nystrom and Berger, *J. Amer. Chem. Soc.*, 1958, **80**, 2896.

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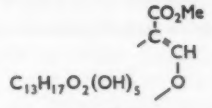
273. *Loganin. Part II.*[1] *Structural Interpretation of the Spectral Properties.*

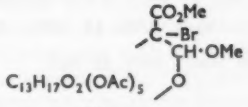
BY A. J. BIRCH and J. GRIMSHAW.

THE conclusions previously [1] drawn from the infrared spectrum of loganin now appear to be erroneous; in particular the small band at 1738 cm.$^{-1}$ thought to indicate the presence of a saturated ester group must have been due to an impurity. On further examination loganin from *Strychnos lucida* R.Br. showed infrared bands at 1710 and 1650 cm.$^{-1}$ which we now assign to an αβ-unsaturated ester carbonyl group and an enol ether group respectively; it has an ultraviolet band at $\lambda_{max.}$ 237 mμ (log ε 4·03) in aqueous solution, attributed to an unsaturated ester group of the type shown in partial structure (I). In view of doubts expressed [2] on the identity of our original material, we believe that these spectra, together with the m. p.s and optical rotations of loganin and its penta-acetyl derivative (cf. refs. 2 and 3) establish that it is in fact loganin.

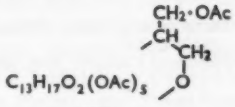
Previously [1] we interpreted the spectra to indicate the presence of an αβ-unsaturated carbonyl function in a five-membered ring, but this is contradicted by our inability to find the expected low-intensity absorption maximum in the region of 300 mμ. The chromophore represented in formula (I), which has been studied for synthetic compounds [4] and is present in plumierid,[5] is, however, in accord with the spectrum of loganin and its presence is supported by the result of reaction of penta-acetyl-loganin with bromine in methanol.



(I)



(II)



(III)

The methyl ether bromide (II) obtained was to be expected from the chemistry of plumierid [5] and aucubin,[6] both of which contain an enol ether group. The methyl ether bromide possesses no absorption maximum between 210 and 300 mμ and one broad absorption

[1] Part I, Birch and Smith, *Austral. J. Chem.*, 1956, **9**, 234.
[2] Mertz and Lehmann, *Arch. Pharm.*, 1957, **290**, 543.
[3] Mertz and Krebs, *Arch. Pharm.*, 1937, **275**, 217.
[4] Bader, *Helv. Chim. Acta*, 1953, **28**, 215; Korte and Buchel, *Angew. Chem.*, 1959, **71**, 709.
[5] Halpern and Schmid, *Helv. Chim. Acta*, 1958, **41**, 1109.
[6] Grimshaw and Juneja, *Chem. and Ind.*, 1960, 656.

band due to double-bond stretching vibrations (ester groups) at 1745 cm.$^{-1}$, thus establishing the relation between the enol ether and the ester group. The difficulty experienced [1,2,3] in hydrogenating the double bond of loganin is also in accord with structure (I) since similar difficulty was encountered with plumierid.[5]

In view of doubts expressed [2] we have confirmed the finding that loganin is the methyl ester of an acid. Alkaline hydrolysis produced loganic acid [1] (norloganin [2]), isolated as the penta-acetyl derivative, $\lambda_{max.}$ 230 mμ (log ε 4·0 in ethanol), $\nu_{max.}$ 3200 (very broad), 1750, 1715, and 1645 cm.$^{-1}$. Brief treatment with methyl iodide and silver oxide re-formed loganin penta-acetate, previously [1] also re-formed by the action of diazomethane. The product of reaction of loganin with lithium in liquid ammonia, isolated as its hexa-acetyl derivative,[1] also supports the formula (I) and the derivative can be assigned the partial structure (III). It shows no infrared absorption due to hydroxyl, has a band at 1740 cm.$^{-1}$ (OAc), and no absorption maximum in the ultraviolet region (210—300 mμ).

It seems clear that the acetaldehyde reported as formed on the ozonolysis of penta-acetyl-loganin [1] in fact came from the ethyl acetate used as solvent, and loganin does not [2] contain an ethylidene residue. Loganin, $C_{17}H_{26}O_{10}$, must contain, in addition to the expanded unit shown (I), a glycoside group, a further hydroxyl group, a carbocylic ring, an ether ring, and a methyl group attached to carbon. In view of the chemical relationship of loganin to plumierid [5] and the occurrence of loganin in *Strychnos* species [7] and aucubin in *Buddleia* species,[8] both belonging to the family of Loganiaceæ, we suggest a biogenetic and therefore structural relation between these compounds. On this basis it is possible to indicate several likely structures for loganin, but we prefer to reserve discussion of these until more experimental evidence is available.

Experimental.—Infrared spectra are quoted for Nujol mulls.

Methylation of penta-acetyl-loganic acid. Penta-acetyl-loganic acid (20 mg.) was dissolved in methyl iodide (3 ml.) and refluxed over silver oxide (30 mg.) for 90 min., then the mixture was diluted with ether and filtered. The filtrate was washed with sodium hydrogen carbonate solution and water and dried (Na_2SO_4), and the solvent removed. The residue crystallised from ethyl acetate–light petroleum (b. p. 60—80°) as needles (15 mg.), m. p. 140—141° undepressed on admixture with loganin penta-acetate, m. p. 141—142°. The two samples showed the same infrared spectrum.

Penta-acetyl-loganin methyl ether bromide (II). Loganin penta-acetate (60 mg.), dissolved in methanol (5 ml.), was cooled to 0° and bromine (16 mg.) in methanol (1·5 ml.) slowly added. The solution was decolorised and gradually deposited needles, m. p. 130—145°. Recrystallisation from ethyl acetate–light petroleum (b. p. 60—80°) afforded *penta-acetyl-loganin methyl ether bromide* as stout needles, m. p. 158—161° (Found: C, 47·5; H, 5·55; Br, 11·5; OMe, 8·9. $C_{28}H_{39}BrO_{16}$ requires C, 47·2; H, 5·5; Br, 11·3; 1OMe, 8·7%).

This work was carried out during the tenure (by J. G.) of an I.C.I. Fellowship. We are indebted to Dr. E. Ritchie for a gift of loganin.

Department of Chemistry, The University, Manchester, 13. [*Received, July 29th*, 1960.]

[7] Dunstan and Short, *Pharm. J. Trans.*, 1883, **14**, 1025; Anet, Hughes, and Ritchie, *Austral. J. Chem.*, 1953, **6**, 58.

[8] Paris and Chaslot, *Ann. pharm. franç.*, 1955, **13**, 648.

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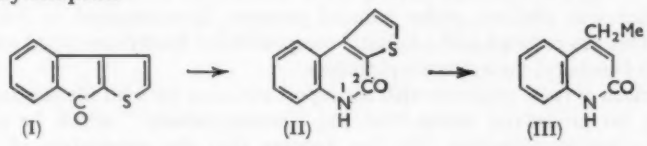
274. *Reactions of Organic Azides. Part X.*[1] *The Schmidt Reaction with 3′-Oxoindeno(2′,1′-2,3)thiophen: the Structure of the Product.*

By C. L. Arcus and G. C. Barrett.

3′-Oxoindeno(2′,1′-2,3)thiophen (I) with hydrazoic acid in trichloroacetic and sulphuric acid at 55° gave material which, on sublimation and recrystallisation from nitrobenzene, yields a single product.[1] Possible structures are thieno(2′,3′-3,4)-2-quinolone (II), formed by migration of the phenylene ring, or the isoquinolone isomer formed by migration of

[1] Part IX, Arcus and Barrett, *J.*, 1960, 2098.

the thieno-ring. The compound was largely unchanged after being heated with aqueous potassium permanganate, even at 250°; but with Raney nickel it was reductively desulphurised to 4-ethylcarbostyril [2] (III) and therefore has structure (II). Migration of the phenylene group is analogous to the migration of phenyl during the Schmidt reaction with 2-benzoylthiophen.[3]



Experimental.—M. p.s are corrected.

Thieno(2′,3′-3,4)-2-quinolone (0·30 g.; m. p. 281°) was heated with potassium permanganate (2·97 g.) in water (30 ml.) during 3 hr. The purple mixture was filtered hot; after being suspended in water saturated with sulphur dioxide, the solid (0·20 g.) had m. p. 278—280°, not depressed by the starting material. The filtrate, after saturation with sulphur dioxide, was cooled and a trace of white solid, m. p. > 280°, was filtered off. The filtrate was acidified with sulphuric acid; ether-extraction yielded a buff solid (0·07 g.), m. p. 178—181°, which contained nitrogen and sulphur but was not further investigated.

An identical mixture, heated at 250° for 3½ hr. and treated as above, returned the starting material, m. p. and mixed m. p. 279—281°.

Raney nickel "C" [4] (1·0 g.) and the thienoquinolone (0·10 g.) were heated under reflux in *m*-xylene (25 ml.) during 6 hr. Evaporation of the filtered mixture yielded 4-ethylcarbostyril (0·07 g.; m. p. 188—190°), that had m. p. 194·5—195·5° after recrystallisation from heptane, addition to alumina in benzene, and elution with benzene containing 10% of ether (Found: C, 75·7; H, 6·15; N, 8·1. Calc. for $C_{11}H_{11}NO$: C, 76·3; H, 6·4; N, 8·1%). This product was identical with 4-ethylcarbostyril, m. p. 197·5° (mixed m. p. 197°; same infrared spectrum), prepared by Wöhnlich's method [2] (Found: C, 76·0; H, 6·6; N, 8·3%).

We thank the Department of Scientific and Industrial Research for a maintenance grant (to G. C. B.) and Imperial Chemical Industries Limited for participation in a grant.

Battersea College of Technology, London, S.W.11.
Dyson Perrins Laboratory, Oxford University. [*Received, August 4th*, 1960.]

[2] Wöhnlich, *Arch. Pharm.*, 1913, **251**, 535.
[3] Badger, Howard, and Simons, *J.*, 1952, 2849.
[4] Hurd and Rudner, *J. Amer. Chem. Soc.*, 1951, **73**, 5157.

275. *Isobutyl and t-Butyl Derivatives of 2-Methoxynaphthalene.*

By R. T. Ferris and D. Hamer.

Isobutylphenols can most satisfactorily be prepared by the Claisen rearrangement of 1-methylallyl phenyl ethers, followed by the reduction of the isobutenylphenol so obtained.[1] We have used this method to prepare 1-isobutyl-2-naphthol and then methylated it to give 1-isobutyl-2-methoxynaphthalene (m. p. 27°). Cahen [2] has reported the preparation of an "isobutylnerolin" by the reaction of isobutyl bromide with nerolin and aluminium chloride in carbon disulphide. A substance with m. p. 66° was obtained, but subsequent work on this type of reaction has suggested that the product might be a t-butyl rather than an isobutyl derivative.[3] Some later work by Bromby, Peters, and Rowe,[4] and by Tsukervanik and Tambortseva,[5] failed to resolve the course of this reaction or the nature of Cahen's product.

We therefore prepared 2- (m. p. 35°) and 3-methoxy-1-t-butylnaphthalene (m. p. 67°)

[1] Bartz, Miller, and Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 371.
[2] Cahen, *Bull. Soc. chim. France*, 1898, **19**, 1007.
[3] Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3276.
[4] Bromby, Peters, and Rowe, *J.*, 1943, 144.
[5] Tsukervanik and Tambovtseva, *Bull. Univ. Asie centrale*, 1938, **22**, 221; *Chem. Abs.*, 1940, **34**, 4729.

XUM

and 1-isobutyl-2-methoxynaphthalene (m. p. 27°). The first was prepared by the Friedel–Crafts reaction of t-butyl chloride and nerolin. The second was made by treating 1-bromo-2-methoxynaphthalene with t-butyl chloride and aluminium chloride, the bromine atom then being removed through the Grignard derivative. The isobutyl compound was prepared by using the Claisen rearrangement referred to above. When 1-methylallyl naphthyl ether was distilled under reduced pressure, it rearranged to 1-isobutenyl-2-naphthol. This was reduced to the isobutyl compound and finally converted with dimethyl sulphate into 1-isobutyl-2-methoxynaphthalene.

A comparison of these products with the report of Cahen (or with the substance isolated by following his procedure) shows that the " isobutylnerolin " which he isolated was 3-methoxy-1-t-butylnaphthalene. It also appears that the orientation of the t-butyl group is very dependent on the reaction conditions.

Experimental.—2-Methoxy-1-t-butylnaphthalene was prepared by the normal Friedel–Crafts reaction between nerolin, t-butyl chloride, and aluminium chloride in ligroin (b. p. 60°). When recrystallised it had m. p. 35° (Found: C, 84·0; H, 8·3. Calc. for $C_{15}H_{18}O$: C, 84·1; H, 8·4%).

3-Methoxy-1-t-butylnaphthalene. 1-Bromo-2-methoxynaphthalene was first prepared by heating nerolin (20 g.) and *N*-bromosuccinimide (9 g.) in carbon tetrachloride (50 ml.) for 8 hr. under reflux.[4] The product recrystallised from ligroin, yielding 10 g. of the bromo-compound. Conversion into 1-bromo-2-methoxy-4-t-butylnaphthalene was accomplished by the Friedel–Crafts reaction: 1-bromo-2-methoxynaphthalene (11·9 g.), t-butyl chloride (4·6 g.), and aluminium chloride (0·22 g.) were heated under reflux in ligroin (15 ml.) for 3 hr. When isolated and recrystallised, 7 g. of product were obtained, having m. p. 78—80° (Found: C, 61·3; H, 5·9; Br, 27·0. Calc. for $C_{15}H_{17}BrO$: C, 61·5; H, 5·8; Br, 27·3%). Finally the 1-bromo-group was removed through hydrolysis of the Grignard derivative. The product from above (7 g.) was dissolved in ether (25 ml.) and reacted with magnesium turnings (0·66 g.) in ether (30 ml.). The resulting solution was heated, hydrolysed, and then distilled under reduced pressure; 3 g. of 3-methoxy-1-t-butylnaphthalene, m. p. 67°, were obtained (Found: C, 83·8; H, 8·2. Calc. for $C_{15}H_{18}O$: C, 84·1; H, 8·4%). The same product was obtained by carrying out the reaction as described by Cahen.

1-Methylallyl 2-naphthyl ether. Naphthol (72 g.), 1-methylallyl chloride (45 g.), and potassium carbonate (70 g.) were refluxed in acetone (75 g.) for 22 hr. with stirring. Water (100 ml.) was then added and the product taken up in ether. This solution was washed with 10% sodium hydroxide solution, then with water, and dried with potassium carbonate. After evaporation of the solvent and purification of the product, 28 g. of *1-methylallyl 2-naphthyl ether* were obtained, with m. p. 49° (Found: C, 84·5; H, 7·2. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

1-Isobutyl-2-methoxynaphthalene. The above isobutenylnaphthol (20 g.) was hydrogenated in dry ethanol (150 ml.) over platinum oxide (0·2 g.) under pressure in a rocking autoclave at 20°. From the resultant solution 15 g. of 1-isobutyl-2-naphthol were obtained (m. p. 34°). This naphthol was shaken in alkali with dimethyl sulphate (6·3 g.). *1-Isobutyl-2-methoxynaphthalene* was filtered off, washed, and recrystallised twice, giving 5 g. of product, m. p. 27° (Found: C, 83·9; H, 8·3. $C_{15}H_{18}O$ requires C, 84·1; H, 8·4%).

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[4] Buu-Hoï, *Annalen*, 1944, **556**, 1.

276. O^2,3′-*Cyclouridine.*

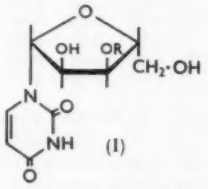
By R. LETTERS and A. M. MICHELSON.

PREVIOUS attempts to convert 3′-*O*-toluene-*p*-sulphonyluridine (I) into the cyclonucleoside (II) by using a number of bases were unsuccessful [1] despite the fact that both 3′,5′-di-*O*-methanesulphonylthymidine and 3′-deoxy-3′-iodothymidine readily gave O^2,3′-cyclonucleoside derivatives.[2] A general method for the preparation of cyclonucleosides from the appropriate methanesulphonyl or toluene-*p*-sulphonyl derivative is now described.

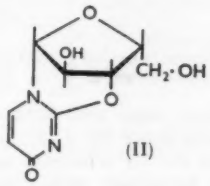
[1] Brown, Parihar, Todd, and Varadarajan, *J.*, 1958, 3028.
[2] Michelson and Todd, *J.*, 1955, 816.

XUM

Sodium t-butoxide (1 mol.) converted 5′-*O*-methanesulphonylthymidine completely into the cyclonucleoside, O^2,5′-cyclothymidine [2] which had been obtained previously only by way of the 5′-deoxy-5′-iodonucleoside. 3′-*O*-Toluene-*p*-sulphonyluridine [1] with sodium



(I)



(II)

R = p-$C_6H_4Me{\cdot}SO_2$

t-butoxide in dimethylformamide gave three products that were detected by paper chromatography. The major product, purified by counter-current distribution, closely resembled O^2,2′-cyclouridine in its paper-chromatographic, paper-electrophoretic, and light-absorption properties (cf. Table 1); it was not oxidised by sodium metaperiodate and we conclude that it is O^2,3′-cyclouridine (II).

3′-*O*-Toluene-*p*-sulphonyluridine with sodium hydroxide gave 3-β-D-xylofuranosyluracil.

TABLE 1. *Light-absorption properties of cyclonucleosides.*

Solvent:	95% EtOH		Water		0·01N-HCl		0·01N-NaOH	
	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)
O^2,2′-Cyclouridine	249, 223	237	250, 222	239	250, 221	234	253, 224	237
O^2,3′-Cyclouridine	230	—	246, 230	240	246, 230	240	253, 225	240
O^2,5′-Cyclothymidine ...	244	221	250	223	252	224	253	226

Experimental.—O^2,3′-*Cyclouridine.* To a solution of 3′-*O*-toluene-*p*-sulphonyluridine [1] (440 mg., 1 mmole) in dimethylformamide (25 c.c.) was added sodium t-butoxide (4 c.c. of an 0·5M-solution in t-butyl alcohol), and the mixture was kept at 100° for 2 hr. Solvent was then removed under reduced pressure and the residue washed with anhydrous ether and then submitted to counter-current distribution (70 transfers) in ethyl acetate and water. The major product was present in the first two tubes, the contents of which were evaporated to dryness. The residue was dissolved in 95% ethanol. Addition of ether precipitated O^2,3′-*cyclouridine* as an amorphous powder which was collected and dried (135 mg., 56%). Traces of sodium toluene-*p*-sulphonate were removed by shaking an aqueous solution of the compound with a mixture of acidic and basic ion-exchange resins. Pure O^2,3′-cyclouridine crystallised from ethanol–ether as needles (Found: N, 11·7. $C_9H_{10}N_2O_5,H_2O$ requires N, 11·5%). Light absorption: in H_2O, $\lambda_{max.}$ 246, 230 mμ (ε 5780, 6900), $\lambda_{min.}$ 240 mμ (ε 5420); in 0·01N-HCl, $\lambda_{max.}$ 246, 230 mμ (ε 5660, 6965), $\lambda_{min.}$ 240 mμ (ε 5250); in 0·01N-NaOH, $\lambda_{max.}$ 253, 225 mμ (ε 5430, 5780), $\lambda_{min.}$ 240 mμ (ε 4905).

5′-O-*Methanesulphonylthymidine.* Methanesulphonyl chloride (1·5 mol.) was added to 3′-*O*-acetylthymidine [3] (0·41 g.) in pyridine (5 c.c.), and the solution kept at 0° overnight. Water (1 c.c.) was then added, the mixture evaporated to dryness, and a solution of the residue in chloroform was washed successively with 0·1N-sulphuric acid, aqueous sodium hydrogen carbonate, and water, then dried (Na_2SO_4), and evaporated. This residue was dissolved in 95% ethanol (10 c.c.), saturated ethanolic ammonia (10 c.c.) was added, and the mixture was left at 0° overnight. Solvent was removed and the final residue recrystallised from ethanol to give 5′-O-*methanesulphonylthymidine* (290 mg.), m. p. 149° (Found: N, 8·7. $C_{11}H_{16}N_2O_7S$ requires N, 8·8%).

Action of sodium t-butoxide on 5′-O-*methanesulphonylthymidine.* Sodium t-butoxide (0·2 c.c. of an 0·5M-solution in t-butyl alcohol; 0·1 mmole) was added to a solution of 5′-*O*-methanesulphonylthymidine (32 mg., 0·1 mmole) in dimethylformamide (1·8 c.c.), and the mixture kept at 100° for 2 hr. Paper chromatography and paper electrophoresis showed complete conversion into O^2,5′-cyclothymidine, identical with an authentic specimen.

Paper chromatography and paper electrophoresis (*Table* 2). Ascending chromatograms on

[3] Michelson and Todd, *J.*, 1953, 951.

TABLE 2.

	R_F A	R_F B	R_F C	Electrophoresis (cm.)
O^2,2′-Cyclouridine	0·16	0·28	0·60	−2
O^2,3′-Cyclouridine	0·16	0·26	0·60	0
Uridine	0·20	0·30	0·60	16
3-β-D-Arabinofuranosyluracil	0·25	0·35	0·63	4·5
3′-*O*-Toluene-*p*-sulphonyluridine + 0·1N-NaOH at 100° for 2 hr.	0·35	0·44	0·63	5·5
3′-*O*-Toluene-*p*-sulphonyluridine	0·85	0·86	0·89	4·5

Whatman no. 1 paper were used with solvent systems: A, butan-1-ol–water (86 : 14); B, butan-1-ol–acetic acid–water (4 : 1 : 5); C, propan-2-ol–aq. 1% $(NH_4)_2SO_4$ (2 : 1). Electrophoresis was carried out on Whatman no. 1 paper with 0·02M-borate buffer, and a voltage gradient of 20 v/cm. for 1½ hr. Migrations toward the anode are tabulated.

With the exception of uridine, all compounds listed gave a negative result with the periodate–Schiff's spray reagent.[4]

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[*Received, September 9th*, 1960.]

[4] Buchanan, Dekker, and Long, *J.*, 1950, 3162.

277. *The Preparation of Some 2-Substituted 9-Diazofluorenes.*

By KEITH D. WARREN.

THIS note describes the preparation, by the method of Nenitzescu and Solomonica,[1] of a number of 2-substituted 9-diazofluorenes (Table 1). Preparation of the corresponding hydrazones (Table 2) led, in four cases, to two products, each of which was oxidised to the same diazo-compound.

TABLE 1. *2-Substituted 9-diazofluorenes.*

Subst.	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
NO_2	55	expl. ~180°	66·15	2·9	18·0	$C_{13}H_7N_3O_2$	65·8	2·95	17·7
NH_2 [a]	70	137·5 † [b]	—	—	—	$C_{13}H_9N_2$	—	—	—
F	73	93·5—94·5	—	—	13·3	$C_{13}H_7FN_2$	—	—	13·3
Cl	65	126·5—127·5 †	68·8	3·3	12·2	$C_{13}H_7ClN_2$	68·8	3·1	12·3
Br	65	138—139 †	57·75	2·9	10·4	$C_{13}H_7BrN_2$	57·6	2·6	10·3
I	69	145·5—146·5 †	49·3	2·4	8·75	$C_{13}H_7IN_2$	49·05	2·2	8·8
OH	15	197—200 ‡	74·8	4·2	13·5	$C_{13}H_8N_2O$	75·0	3·9	12·5
OMe	56	126—127 †	75·6	4·5	12·7	$C_{14}H_{10}N_2O$	75·7	4·5	12·6
OEt	66	118—119	76·4	5·1	11·9	$C_{15}H_{12}N_2O$	76·3	5·1	11·9
CN	80	(117—118) 126—127 [c]	77·3	3·5	19·3	$C_{14}H_7N_3$	77·4	3·25	19·3

[a] Not new. † Melts with decomp. ‡ Decomp. without melting.
[b] Rapid heating: slow heating, decomp. 140—142°. [c] Bennett and Noyes (*Rec. Trav. chim.*, 1929, **48**, 895) give 137°. [c] Two crystal forms.

Experimental.—M. p.s are corrected.

Hydrazones. The appropriate ketone was heated under reflux with a slight excess of 100% hydrazine hydrate solution, in alcohol. The product was recrystallised from the minimum volume of that solvent.

Diazo-compounds. The hydrazone was shaken with yellow mercuric oxide (excess) and anhydrous sodium sulphate for 4 hr. in anhydrous ether containing ethanolic potassium hydroxide. The product from the ethereal solution was recrystallised from low-boiling light petroleum.

2-Ethoxyfluorenone. 2-Hydroxyfluorenone (9 g.) and sodium hydroxide (2·5 g.) in "AnalaR" acetone (280 ml.) were heated under reflux for 1 hr., ethyl bromide (7·85 g.) being added during 15 min. and heating continued for 24 hr. After filtration and reduction to 50 ml., the solution was poured into 10% aqueous sodium hydroxide (1·5 l.). The resulting solid, after recrystallisation from alcohol (charcoal) and chromatography in benzene on neutral alumina, gave *2-ethoxyfluorenone* as light orange needles (from light petroleum), m. p. 94·5—95° (3·5 g., 38%) (Found: C, 80·6; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·35; H, 5·4%).

[1] Nenitzescu and Solomonica, *Org. Synth.*, Coll. Vol. II, p. 496.

TABLE 2. *2-Substituted fluorenone hydrazones.*

Subst.	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
NO_2 *	65	228—230° ‡ [a]	65·4	3·6	17·3	$C_{13}H_9N_3O_2$	65·3	3·8	17·6
NH_2 *	82	206—207 [b]	—	—	—	$C_{13}H_{11}N_3$	—	—	—
F	69	176—177 †	—	—	13·35	$C_{13}H_9FN_2$	—	—	13·2
Cl	72	131—132	68·6	3·9	11·9	$C_{13}H_9ClN_2$	68·3	3·9	12·2
Br	80	126—127 ‡	57·4	3·4	10·2	$C_{13}H_9BrN_2$	57·1	3·3	10·3
I	71	161·5—163·5	49·0	2·9	8·95	$C_{13}H_9IN_2$	48·75	2·8	8·75
		141·5—143 ‡	—	—	—	"	—	—	—
OH *	51	205—207 ‡ [a]	—	—	—	$C_{13}H_{10}N_2O$	—	—	—
OMe	52	136·5—138	74·8	5·2	12·7	$C_{14}H_{12}N_2O$	75·0	5·4	12·5
		97—100	—	—	—	"	—	—	—
OEt	67	155—157 †	75·4	5·6	11·75	$C_{15}H_{14}N_2O$	75·6	5·9	11·8
		145—147	—	—	—	"	—	—	—
CN	65	209—211 †	76·5	4·25	19·0	$C_{14}H_9N_3$	76·7	4·1	19·2
		180—182 †	—	—	—	"	—	—	—

*†‡ See Table 1. [a] Gerhardt (*Monatsh.*, 1920, **41**, 199) gives m. p. 214°. [b] Bennett and Noyes (footnote *b*, Table 1) give 209°. [c] Gerhardt (footnote *a*) gives m. p. 201—202°.

2-Cyanofluorenone. This was prepared according to Dickinson and Eaborn's method; it formed yellow-brown needles (from light petroleum, then alcohol), m. p. 182—183° (lit.,[2] 173°). The identity of the product was established by acid-hydrolysis to fluorenone-2-carboxylic acid (yield 83%).

Except for the fluorine-containing compounds, analyses were by Mr. J. M. L. Cameron and his staff.

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[2] Dickinson and Eaborn, *J.*, 1959, 2337.

278. *Kinetics of the Alkaline Hydrolysis and Bromination of Bromoform.*

By R. P. BELL and M. H. FORD-SMITH.

IN studying the bromination of acetaldehyde and acetone in aqueous alkali, giving bromoform, we have made some kinetic measurements on the subsequent bromination and hydrolysis of bromoform. The alkaline hydrolysis of the haloforms in aqueous dioxan has been studied extensively by Hine and his co-workers.[1] They find that the rate of deuterium exchange is very much greater than the rate of hydrolysis under the same conditions, and on this basis propose the mechanism:

(i) $CHBr_3 + OH^- \rightleftharpoons CBr_3^- + H_2O$ (Fast)

(ii) $CBr_3^- \longrightarrow CBr_2 + Br^-$ (Rate-determining)

(iii) $\left\{\begin{array}{l} CBr_2 + 2OH^- \longrightarrow CO + H_2O + 2Br^- \\ CBr_2 + 3OH^- \longrightarrow HCO_2^- + H_2O + 2Br^- \end{array}\right\}$ (Fast

The analogous species CCl_2 is believed to occur in the thermal decomposition of chloromethanes.[2] We have found that bromoform reacts slowly with alkaline aqueous hypobromite solution according to the equation $CHBr_3 + BrO^- \longrightarrow CBr_4 + OH^-$, carbon tetrabromide (m. p. 49°) being deposited in good yield. The experiments described below show that the reaction is of zero order with respect to hypobromite, and of first order with respect to both bromoform and hydroxide ions: the second-order velocity constant at 25·2° is $3·1 \pm 0·3 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. The hydrolysis of bromoform has been studied under the same conditions, giving a velocity constant $2·7 \pm 0·1 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$, *i.e.*, the velocities of the two processes are the same within experimental error. Hypobromite does not react with formate ion or with carbon monoxide under these conditions, so that the rate-determining step in the bromination of bromoform must also be reaction

[1] Hine, Dowell, and Singley, *J. Amer. Chem. Soc.*, 1956, **78**, 479; Hine, Burske, Hine, and Langford, *ibid.*, 1957, **79**, 1406.

[2] Shilov and Sabirova, *Zhur. fiz. Khim.*, 1960, **34**, 860.

(ii) above, followed by the rapid reaction $CBr_2 + BrO^- + Br^- + H_2O \longrightarrow CBr_4 + 2OH^-$. It thus appears that the species CBr_3^- does not react rapidly with hypobromite.

Experimental.—Bromoform was distilled under reduced pressure and stored in the dark, freshly prepared aqueous solutions being used. Hypobromite solutions were prepared by dissolving bromine in an excess of sodium hydroxide, and were estimated iodometrically. In the kinetic measurements the initial concentrations were $[OH^-] = 0{\cdot}1$—$0{\cdot}5$M, $[OBr^-] = 0{\cdot}0022$M, $[CHBr_3] = 0{\cdot}001$—$0{\cdot}003$M. The reaction was followed by measuring the absorption due to hypobromite ion with a S.P. 500 Unicam spectrophotometer (1 cm. silica cell in holder at $25{\cdot}2° \pm 0{\cdot}1°$). Hypobromite was found to have maximum absorption at 3300 Å with $\varepsilon = 301 \pm 0{\cdot}5$ (mean of 15 measurements): this is in good agreement with the measurements by Farkas and Klein [3] ($\lambda = 3300$ Å, $\varepsilon = 300$) but differs from those by Anbar and Dostrovsky [4] ($\lambda = 3330$ Å, $\varepsilon = 180$). There is no appreciable absorption at this wavelength by bromoform, carbon tetrabromide, bromide, or hydroxide. The concentration of hydroxide ions does not change significantly during an experiment, and plots of log $[CHBr_3]$ against time were linear, showing that the reaction is of zero order with respect to hypobromite and of first order with respect to bromoform. The second-order constants were obtained by dividing the slopes of these plots by $0{\cdot}434[OH^-]$; the mean of six experiments was $k = 3{\cdot}1 \pm 0{\cdot}3 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

The rate of hydrolysis was measured under the same conditions, but with the omission of hypobromite, the reaction being followed by the absorption due to bromoform. This has a maximum at $\lambda = 2205$ Å ($\varepsilon = 1900$), but this wavelength could not be used because of strong absorption by bromide and hydroxide. Measurements were made at 2550 or 2650 Å, and the concentration of bromoform remaining assumed proportional to $D_t - D_\infty$, where D is the optical density. The mean of three experiments was $k = 2{\cdot}7 \pm 0{\cdot}1 \times 10^{-4}$ l. mole sec.$^{-1}$. This value differs little from that obtained by Hine *et al.*[1] ($3{\cdot}2 \times 10^{-4}$) for alkaline hydrolysis in 67% aqueous dioxan.

The rather large experimental error in these velocity constants is due to slight decomposition or evaporation of bromoform solutions, and deposition of solid carbon tetrabromide or evolution of carbon monoxide in the later stages of the reaction.

We thank the Department of Scientific and Industrial Research for a Research Studentship awarded to M. H. F.-S.

PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, September 27th*, 1960.]

[3] Farkas and Klein, *J. Chem. Phys.*, 1948, **16**, 886.
[4] Anbar and Dostrovsky, *J.*, 1954, 1105.

279. *Preparation of Polychlorobenzylamines.*

By J. S. MORLEY.

THE mono-, five of the six possible di-, five of the six possible tri-, 2,3,4,5-tetra-, and 2,3,4,5,6-penta-chlorobenzylamines have been prepared in good yield from the corresponding chlorobenzyl bromides or chlorides by way of the quaternary salts, $(Ar{\cdot}CH_2{\cdot}C_6H_{12}{\cdot}N_4)^+X^-$, formed with hexamine. Conversion of these salts into benzylamines [1,2] was smooth with 4 or more molar proportions of a strong acid. When less acid or a weaker acid was used, conversion into benzaldehydes occurred [3] except where two *o*-chloro-substituents were present. In these cases only benzylamines were formed even on boiling the salts in water.[4]

Experimental.—Preparation of toluenes. 2,6-Dichlorotoluene was available commercially. The following toluenes were prepared by recorded methods: 2,3-,[5] 2,5-dichloro-,[6] 2,3,6-,[7]

[1] Delépine, *Bull. Soc. chim. France*, 1895, **13**, 358.
[2] Galat and Elion, *J. Amer. Chem. Soc.*, 1939, **61**, 3585.
[3] Sommelet, *Compt. rend.*, 1913, **157**, 852.
[4] Cf. Angyal, Morris, Rassack, and Waterer, *J.*, 1949, 2704.
[5] Marvel, Overberger, Allen, Johnston, Saunders, and Young, *J. Amer. Chem. Soc.*, 1946, **68**, 861.
[6] Crauw, *Rec. Trav. chim.*, 1931, **50**, 772.
[7] Brimelow, Jones, and Metcalfe, *J.*, 1951, 1208.

Benzylamines.

Subst.	Base, b. p./mm.	Hydrochloride (m. p.)	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
o-Cl	219°/749 [a]		86							
m-	226—228°/749 [b]		95							
p-	222—224°/765 [c]		85							
2,3-Cl_2	136—140°/18	266—267° [l]	100	39·2	3·8	6·7				
2,4-	132°/20 [d]	279—280 [e, m]	89	39·6	3·7	6·3				
2,5-	124—126°/13	259—260 [l]	99	39·6	3·8	6·3	$C_7H_7NCl_2$,HCl	39·6	3·8	6·6
2,6-	117°/10	237—238 [f]	93	39·9	3·8	6·6				
3,4-	137—139°/15 [g]	239—240 [h, n]	87	40·1	3·8	6·8				
2,3,5-Cl_3	M. p. 59—59·5° [p]		91	39·5	2·8	6·8				
2,3,6-	146—147°/10 [i]		95	40·4	2·9	6·7	$C_7H_6NCl_3$	40·0	2·9	6·7
2,4,5-	M. p. 59—60° [p]		85	39·8	2·9	6·7				
2,4,6-	M. p. 62—63° [j, p]	247—248 [k]	89	39·5	2·7	6·6				
3,4,5-		271—272 [n]	80	33·6	2·9	5·4	$C_7H_6NCl_3$,HCl	34·0	2·9	5·7
2,3,4,5-Cl_4	M. p. 90—91° [p]	>300 [n]	46	33·9	1·9	5·8	$C_7H_5NCl_4$	34·3	2·0	5·7
2,3,4,5,6-Cl_5	M. p. 139—140° [p]		43	30·2	1·5	4·9	$C_7H_4NCl_5$	30·1	1·4	5·0

[a] Graymore and Davies (*J.*, 1945, 293) give b. p. 220°/775 mm. [b] Graymore and Davies (*loc. cit.*) give b. p. 226°/760 mm. [c] Graymore and Davies (*loc. cit.*) give b. p. 218—224°/775 mm. [d] Sasa (*J. Soc. Org. Synthet. Chem., Japan*, 1954, **12**, 24) gives b. p. 127—132°/21·5—22 mm.; Surrey and Lesher (*J. Amer. Chem. Soc.*, 1956, **78**, 2573) give b. p. 140°/122 mm. [e] Sasa (*loc. cit.*) gives m. p. 262—263°; Surrey and Lesher (*loc. cit.*) give m. p. 282·1—284·3°; Speziale and Hamm (*J. Amer. Chem. Soc.*, 1956, **78**, 2556) give m. p. 270—272°. [f] Angyal, Morris, Rassack, and Waterer (*J.*, 1949, 2704) give m. p. 237—238°. [g] Surrey and Lesher (*loc. cit.*) give b. p. 139—140°/17 mm. [h] Speziale and Hamm (*loc. cit.*) give m. p. 237—239°. [i] The base slowly crystallised. One recrystallisation from light petroleum gave colourless prisms, m. p. 43—44°. Brimelow, Jones, and Metcalfe (*J.*, 1951, 1208) give b. p. 144°/12 mm. and m. p. 43—44°. [j] Graf, Perathoner and Tatzel (*J. prakt. Chem.*, 1936, **146**, 88) give m. p. 62°. [k] Graf, Perathoner, and Tatzel (*loc. cit.*) give m. p. 247°. [l] Crystallised from ethanol–ether. [m] Crystallised from ethanol. [n] Crystallised from water. [p] Colourless prisms or needles from light petroleum.

2,4,5-,[7] and 3,4,5-trichloro-,[8] 2,3,4,5-tetrachloro-,[9] 2,3,4,5,6-pentachloro-.[10] 2,3,5-Trichlorotoluene was obtained in 90% yield from 2-amino-3,5-dichlorotoluene (a by-product in the manufacture of 2-amino-5-chlorotoluene) by the Sandmeyer reaction. 2,4,6-Trichlorotoluene was prepared from 3-amino-2,4,6-trichlorotoluene [8] as follows: A suspension of the finely divided amine (1 mole) in 6N-hydrochloric acid (4 moles) was diazotised at 0—10° with a concentrated aqueous solution of sodium nitrite (1·1 moles). The filtered diazonium solution was treated with 50% (w/w) hypophosphorous acid (15 moles) in a 10-l. beaker and the mixture was left at room temperature overnight. Pure 2,4,6-trichlorotoluene (75% yield), m. p. 32—33°, separated and was collected and dried at room temperature.

Preparation of benzyl halides. *o*- and *p*-Chloro- and 2,4- and 3,4-dichlorobenzyl chloride, and *m*-chlorobenzyl bromide were available commercially. The following benzyl bromides were prepared by adding bromine (1·05 mole) dropwise to the corresponding toluenes (1·0 mole) (temperature as stated) at a rate compatible with the rate of absorption of the bromine, and then distilling the product under reduced pressure (figures in parentheses are temperature of reaction, b. p. of product, and % yield respectively): 2,3- (140—160°; 140—144°/31 mm.; 74), 2,5- (140—160°; 134—138°/14 mm.; 72), and 2,6-dichloro- (160—170°; 133—135°/10 mm.; 96), 2,3,5- (140—160°; 150—160°/12 mm.; 90), 2,3,6- (140—160°; 156—160°/10 mm.; 91), 2,4,5- (140—160°; 158—160°/10 mm.; 36), 2,4,6- (160—165°; 146—150°/11 mm.; 87), 3,4,5-trichloro- (160—165°; 154—170°/9 mm.; 89), 2,3,4,5-tetrachloro- (150—160°; 180—190°/13 mm.; 68), 2,3,4,5,6-pentachloro- (230°; 204—210°/13 mm.; 94). The crude distilled products (usually highly lachrymatory, low-melting, colourless solids) were used without further purification. 2,3,4,5,6-*Pentachlorobenzyl bromide* separated from ethanol or light petroleum (b. p. 60—80°) in colourless plates, m. p. 116—117° (Found: C, 24·9; H, 0·6. $C_7H_2BrCl_5$ requires C, 24·5; H, 0·6%).

Preparation of benzylamines. Solutions of the appropriate crude benzyl bromide or chloride (1 mole) and hexamine (1·1 mol.) in chloroform were mixed, and the mixture was left at room temperature for 18—24 hr. The benzyl hexammonium salt was collected, washed with chloroform, dried at 40°, then added to 6N-hydrochloride acid (4·4 mol.). The mixture was shaken for 5 min. at room temperature, heated rapidly to the b. p. and steam-distilled until no more

[8] Cohen and Dakin, *J.*, 1902, **81**, 1337.
[9] Cohen and Dakin, *J.*, 1906, **89**, 1453.
[10] Fichter and Glantzstein, *Ber.*, 1916, **49**, 2473.

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formaldehyde distilled over. The benzylamine hydrochloride (contaminated with a little of the benzylamine hydrobromide when a benzyl bromide was used as starting material) separated on cooling or occasionally during the steam-distillation. The benzylamine could be isolated as such by cold filtration without appreciable loss of yield. However, it was usually more convenient to add the hot solution from the steam-distillation to stirred 40% aqueous sodium hydroxide and ice and then to isolate the base by filtration or by extraction with ether. Yields in the Table refer to distilled or once-crystallised material. The hydrochlorides were prepared by adding ether saturated with hydrogen chloride to a solution of the base in acetone, or by recrystallisation of the crude hydrochloride isolated directly from the reaction in methanol–ether saturated with hydrogen chloride.

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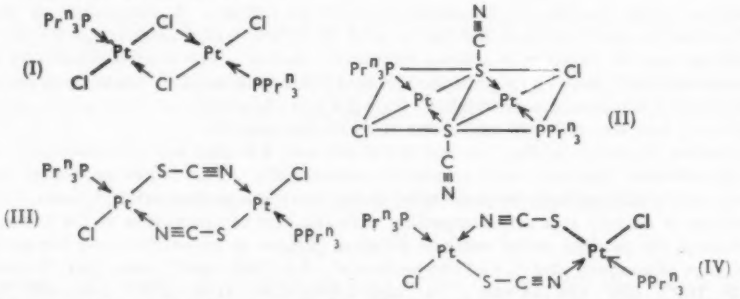
280. *Thiocyanato-bridged Complexes of Platinum*(II).

By J. CHATT and F. A. HART.

THE two isomeric forms of dichlorodithiocyanatobis(tripropylphosphine)diplatinum, $[Pt_2Cl_2(SCN)_2(PPr^n_3)_2]$, have been briefly described and their structures have been discussed.[1-3] This Note gives a fuller account of the preparation and properties of these compounds and describes two isomeric tetrathiocyanato-complexes, $[Pt_2(SCN)_4(PPr^n_3)_2]$.

When di-μ-chlorodichlorobis(tripropylphosphine)diplatinum (I) is treated in cold acetone solution with two molecular proportions of potassium thiocyanate, yellow α-$[Pt_2Cl_2(SCN)_2(PPr^n_3)_2]$ is obtained; the same reaction, carried out in the boiling solvent, gives the pale greenish-yellow β-compound. These compounds are dimeric in boiling benzene and non-electrolytes in nitrobenzene. The small dipole moments in benzene solution (α-compound, 1·57 D; β-compound, 1·36 D) correspond to *trans*-configuration. The only chemically reasonable structures consistent with these facts and with the infrared spectra are (II), (III), and (IV).



X-Ray crystallography shows that the α-isomer has structure (III),[3,4] and that the β-isomer has structure (IV).[5] It had previously been assumed that the thiocyanato-bridge was of the type shown in (II) corresponding to the very stable mercapto-bridge —S(R)→,[6] but it now seems probable that in the great majority of bridged complex thiocyanates, bridging takes place through both the sulphur and the nitrogen atoms. There is no established example where bridging occurs only through the sulphur atom, but in crystalline $AgSCN(PPr^n_3)$ it has been shown that the thiocyanate group links three silver atoms, two through sulphur and one through nitrogen.[7]

We were originally[1] unable to detect isomerism in the tetrathiocyanate

[1] Chatt and Hart, *Nature*, 1952, 673.
[2] Chatt and Duncanson, *Nature*, 1956, 997.
[3] Chatt, Duncanson, Hart, and Owston, *Nature*, 1958, 43.
[4] Owston and Rowe, *Acta Cryst.*, 1960, **13**, 253.
[5] Bland and Owston, personal communication.
[6] Chatt and Hart, *J.*, 1953, 2363.
[7] Turco, Panattoni, and Frasson, *Nature*, 1960, **187**, 772.

$[Pt_2(SCN)_4(PPr^n_3)_2]$, but have now identified two isomers, a yellow α-compound and a white β-compound. The isomerism does not, however, appear to be of the same type as in the dithiocyanato-compounds. In solution, each is converted into a mixture of the two forms. The β-compound has been obtained pure, but the α-compound only as a mixture with the β-compound. The dipole moment of the β-compound is about 2·8 D, which is consistent with a structure analogous to (III) or (IV), the increase of moment over the dithiocyanate complexes being due to free rotation of the terminal thiocyanato-groups. As equilibrium with the α-isomer is reached after 19 hr., the apparent moment rises to 4·9 D, indicating that the α-isomer has a *cis*-configuration, but its exact structure is uncertain.

Experimental.—*α-Di-μ-thiocyanatodichlorobis(tripropylphosphine)diplatinum.* A solution of the tetrachloro-compound (I) (5 g.) in acetone (300 c.c.) was treated at −2° with a solution of potassium thiocyanate (1.14 g., 2 mol.) in acetone (20 c.c.). The solution was evaporated to dryness at 12 mm. The residue was dissolved in chloroform (14 c.c.), the solution filtered, and precipitation effected by ether (85 c.c.). The yellow crystalline product was collected (4·70 g., 89%) and had m. p. 151—154° (decomp.; immersion at 135°). A further precipitation from chloroform–ether followed, and the product was dissolved in warm benzene (120 c.c.), from which it slowly crystallised as yellow prisms on addition of light petroleum (b. p. 80—100°; 120 c.c.). This product had m. p. 144—152° (decomp.; immersion at 135°), unchanged by another similar crystallisation, which gave 2·31 g. of the pure *compound* (Found: C, 27·1; H, 4·7; N, 3·3%; *M*, ebullioscopically in 2·37% benzene solution, 857; in 3·69% solution, 932. $C_{20}H_{42}Cl_2N_2P_2Pt_2S_2$ requires C, 26·8; H, 4·7; N, 3·1%; *M*, 898). In the infrared spectrum, ν_{CN} occurred at 2162 cm.$^{-1}$.

β-Di-μ-thiocyanatodichlorobis(tripropylphosphine)diplatinum. A boiling solution of the tetrachloro-compound (I) (5 g.) in acetone (75 c.c.) was treated with a boiling solution of potassium thiocyanate (1·14 g., 2 mol.) in acetone (15 c.c.). The solution was boiled under reflux for 16 hr., then concentrated to half volume, filtered, and cooled. The *product* (4·79 g.) recrystallised from acetone (225 c.c.) as pale lemon-yellow prisms (2·76 g.), m. p. 167·5—169°. Again recrystallised from acetone, they had m. p. 174·5—175·5° (immersion at 170°), unchanged by further recrystallisation (Found: C, 26·7; H, 4·7; N, 3·3%; *M*, ebullioscopically in 3·08% benzene solution, 922; in 5·17% solution, 920).

α- and β-Di-μ-thiocyanatodithiocyanatobis(tripropylphosphine)diplatinum. (*a*) Preparation from the tetrachloro-compound (I). A solution of compound (I) (2 g.) in acetone (50 c.c.) was treated with a solution of potassium thiocyanate (1·00 g., 4·4 mol.) in acetone (60 c.c.), boiled under reflux for 1 hr., and evaporated to dryness at 12 mm. The residue was taken up in chloroform (25 c.c.), filtered, boiled under reflux for 2 hr., and finally concentrated to 10 c.c. Ether (6 c.c.) was added to the cooled solution, giving pale yellow crystals (1·02 g.), m. p. 180—183° (decomp.). A further quantity (0·26 g.) of this material was obtained from the mother-liquor. These two products were dissolved in chloroform (5 c.c.) and precipitated as crystals by addition of ether (10 c.c.). This purification was repeated twice, giving 0·67 g. of product, m. p. 172—179° (immersion at 170°), which was the pale yellow mixed α- and β-tetrathiocyanato-compounds (Found: C, 28·0; H, 4·6; N, 6·0%; *M*, ebullioscopically in 0·42% chloroform solution, 853; in 0·80% solution, 869. Calc. for $C_{22}H_{42}N_4P_2Pt_2S_4$: C, 28·0; H, 4·5; N, 5·9%; *M*, 943). This sample was quickly extracted with chloroform (2 c.c.) and then shaken for 4 hr. with ethyl methyl ketone (3 c.c.); the residue (0·44 g.), m. p. 189—190·5°, was the more-slowly soluble white *β-tetrathiocyanato-compound* (Found: C, 28·2; H, 4·6; N, 6·3%; *M*, in 1·42% ethyl methyl ketone solution, 965). The pure β-compound showed peaks in the infrared spectrum due to ν_{CN} at 2182 and 2105 cm.$^{-1}$, and the mixed α- and β-compounds also had a peak at 2166 cm.$^{-1}$.

(*b*) Preparation from the α-dithiocyanate (III). A suspension of compound (III) (0·528 g.) in acetone (50 c.c.) and benzene (5 c.c.) was shaken with a solution of potassium thiocyanate (0·114 g., 2 mol.) in acetone (5 c.c.). The complex dissolved and the solution was allowed to evaporate to dryness during 24 hr. The residue, after being washed with water and dried, was divided into halves. One was crystallised from chloroform–ether, giving the mixed α- and β-tetrathiocyanato-compounds, m. p. 175·5—178° (immersion at 160°), identified by mixed m. p. with the compound prepared as in (*c*) below, by nitrogen analysis (Found: N, 5·75%), and by its infrared spectrum, which included peaks at 2182 and 2166 cm.$^{-1}$, the former being the stronger. The second half was boiled in chloroform (3 c.c.) for 3 hr. before precipitation

by ether (10 c.c.). This treatment gave a product, m. p. 176·5—179° (immersion at 160°), identified as mixed α- and β-tetrathiocyanates by its infrared spectrum, the band at 2182 due to the β-isomer being in this case weaker than that at 2166 cm.$^{-1}$.

(*c*) Preparation from the β-dithiocyanate (IV). A suspension of the β-dithiocyanate (0·23 g.) in acetone (8 c.c.) was shaken with a solution of potassium thiocyanate (0·050 g., 2 mol.) in acetone (2 c.c.). The complex at once dissolved and the mixture was stored at 15° for 69 hr. (if the prolonged storage is neglected, only a small yield is obtained). It was then allowed to evaporate to dryness, and the residue was crystallised from chloroform–ether, giving cream-coloured crystals (0·16 g.), m. p. 172·5—174° (immersion at 160°). These were the mixed α- and β-tetrathiocyanato-compounds, identified by analysis (Found: C, 28·0; H, 4·6%) and by infrared spectrum which included peaks at 2182 and 2166 cm.$^{-1}$, the former being the stronger.

Conductivities in nitrobenzene solution. The four thiocyanato-compounds described above are non-electrolytes in nitrobenzene solution.

Dipole moments. These were measured as described previously,[6] except that a platinum-plated glass cell of *ca.* 8 c.c. capacity was used in the dielectric-constant determinations of the tetrathiocyanato-compounds. These were carried out by using very dilute solutions because of insolubility, which also made it impossible to determine the density and refractivity terms in the case of the tetrathiocyanato-compounds; these were estimated, very probably with small error. It is impossible to make a precise allowance for the atom polarisation of metallic complexes; this quantity depends upon the type of complex, and in the present work the value ${}_{A}P = 15\%$ of ${}_{E}P$ is used. Measurements are recorded in the Table: ω is the weight fraction of solute, $\Delta\varepsilon = \varepsilon_S - \varepsilon_B$ where ε_S = dielectric constant of solution, ε_B = dielectric constant of benzene; and similarly for Δv and Δn, where v = specific volume and n = refractive index of the solution.

$10^3\omega$	$10^3\Delta\varepsilon$	$10^3\Delta n$	$-\Delta v/\omega$	${}_{T}P$	${}_{E}P$	${}_{O}P$	μ
α-$Pt_2Cl_2(SCN)_2(PPr^n_3)_2$, yellow.							
7·983	6·383	0·523					
7·113	5·505						
			0·60	279	194	56	1·66
β-$Pt_2Cl_2(SCN)_2(PPr^n_3)_2$, pale greenish-yellow.							
6·640	4·569						
10·064	7·502						
11·445		0·8004					
			0·61	264	195	40	1·40
β-$Pt_2(SCN)_4(PPr^n_3)_2$, white.							
0·761	1·05,* 2·45 †						
0·915	1·41,* 3·12 †						
				412 *	214	166 *	2·8 *
				739 †	214	493 †	4·9 †

* Extrapolated to zero time. † After 19 hr.

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[*Received, October 6th,* 1960.]

281. *Some Observations on Rhodium–Olefin Complexes.*

By M. A. BENNETT and G. WILKINSON.

IN a previous paper,[1] complexes formed by norbornadiene (bicyclo[2,2,1]hepta-2,5-diene) with platinum(II), palladium(II), rhodium(I), and ruthenium(II) were described, and it was suggested that their structures were analogous to those of the corresponding complexes formed by cyclo-octa-1,5-diene.[2] Further evidence for the existence of halogen bridges in the binuclear complex of norbornadiene with rhodium(I), $[C_7H_8RhCl]_2$, is now provided. The compound reacts smoothly in the cold with a number of ligands, giving mononuclear complexes according to the reaction:

$$[C_7H_8RhCl]_2 + 2L \longrightarrow 2C_7H_8RhClL$$

Analytical data and m. p.s for some of these complexes are given in the Table. This

[1] Abel, Bennett, and Wilkinson, *J.*, 1959, 3178.
[2] Chatt and Venanzi, *J.*, 1957, 4735.

" bridge-splitting " reaction has previously been noted for the corresponding cyclo-octa-1,5-diene complex of rhodium(I),[2] and for binuclear olefin complexes of platinum(II) and palladium(II) which are believed to contain halogen bridges.[3]

L in compound C_7H_8RhClL	Appearance	M. p.	Found C (%)	Found H (%)	Found N, P, As or Sb (%)	Found *M*	Required C (%)	Required H (%)	Required N, P, As or Sb (%)	Required *M*
p-Toluidine	Flaky yellow crystals	187—189° *	49·5	5·1	4·0	—	49·8	5·1	4·1	—
Ph_3P	Fine yellow crystals	163—164	60·9	5·0	6·4	487	60·1	4·7	6·3	493
Ph_2MeP	Orange crystals	>150 *	55·5	5·3	—	—	55·8	4·9	—	—
Ph_3As	Orange crystals	183 *	55·5	4·9	14·5	527	55·9	4·3	14·0	537
Ph_3Sb	Red crystals	>100 *	52·1	4·4	—	—	51·4	4·0	—	—

* With decomp.

The new *complexes* are fairly stable in solution in organic solvents, although the triphenylstibine compound decomposes readily in hot solvents and could not be recrystallised. It may be noted that in the corresponding series of cyclo-octa-1,5-diene complexes with P, As, and Sb as donor atoms, only the triphenylphosphine compound was stable enough to be isolated, and this is in agreement with other evidence that norbornadiene is notably more powerful than cyclo-octa-1,5-diene in its complex-forming properties.

Attempts to obtain norbornadiene complexes of rhodium(III) by addition of bromine to the mononuclear rhodium(I) compounds were unsuccessful; compounds were obtained which contained no co-ordinated olefin, as indicated by the infrared spectrum. Although rhodium(III) is isoelectronic with ruthenium(II), which is now known to form olefin complexes,[1,4] the increased positive charge and decreased size of the cation presumably contract the metal orbitals sufficiently to prevent good overlap between them and those of the olefin.

The high-resolution nuclear magnetic resonance spectrum of the recently prepared cyclo-octatetraene complex of rhodium(I), $[C_8H_8RhCl]_2$,[1] shows two main peaks at $\tau =$ 5·8 and 4·3 (measured on a Varian spectrometer at 56·4 cycles in carbon disulphide solution, relative to tetramethylsilane as internal reference), each peak showing some poorly resolved fine structure. This is in contrast to cyclo-octatetraene itself, in which the tub-form is believed to be present,[5] and to $C_8H_8Fe(CO)_3$, in which the ring may be planar,[6] since both show only one proton resonance (at τ 5·48 and 6·49, respectively). Clearly, the tub-form of cyclo-octatetraene must be present also in $[C_8H_8RhCl]_2$, and co-ordination from two non-conjugate double bonds is obviously sufficient to differentiate between the protons in the 8-membered ring. The same is probably true of $C_8H_8PtI_2$ [7] and $C_8H_8RuCl_2$,[4] but these compounds were not sufficiently soluble in organic solvents for measurement of nuclear magnetic resonance. The result shows that, even though the olefin formally supplies four π-electrons in each case, there is a notable difference in bonding between cyclo-octatetraene and the metal in $C_8H_8Fe(CO)_3$ on the one hand, and $[C_8H_8RhCl]_2$ and also π-$C_5H_5CoC_8H_8$—which has also been shown recently [8] to have two proton resonance lines for the C_8H_8 residue—on the other.

Experimental.—Norbornadienerhodium(I) chloride (0·3 g.) in dichloromethane (10 ml.) was treated with the stoicheiometric quantity of the ligand in the same solvent, and the mixture shaken for 15 min. Solvent was removed at 20°/15 mm.; the yellow or orange crystals were recrystallised from ethanol or 1 : 1 benzene–light petroleum (b. p. 40—60°) and vacuum-dried. The *p*-toluidine compound was obtained analytically pure after the crude product had been washed with ether (3 × 15 ml.) and vacuum-dried.

Cyclo-octatetraenerhodium chloride was prepared as previously described,[1] except that the temperature of the reactants was kept between 0° and 50°, instead of at room temperature. This gave higher yields of the complex and prevented deposition of rhodium metal.

[3] Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496, 3413.
[4] Bennett and Wilkinson, *Chem. and Ind.*, 1959, 1516.
[5] Bastiansen, Hedberg, and Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311, and references quoted therein.
[6] Manuel and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366; Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1959, **32**, 880; Rausch and Schrauzer, *Chem. and Ind.*, 1959, 957; Cotton, *J.*, 1960, 400.
[7] Jensen, *Acta Chem. Scand.*, 1953, **7**, 868.
[8] Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1960, **33**, 425.

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We thank the Department of Scientific and Industrial Research for a studentship (to M. A. B.), Messrs. Johnson, Matthey and Co. Ltd. for the loan of rhodium, the Hercules Powder Company for research expenses, and Dr. L. Pratt for assistance with nuclear magnetic resonance measurements.

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IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, October 21st*, 1960.]

282. *Polarographic Behaviour of 2-Methyl-1,2-di-3′-pyridylpropan-1-one.*

By M. J. ALLEN and J. VIKIN.

RECENTLY the polarographic estimation of 2-methyl-1,2-di-3′-pyridylpropan-1-one [1] has been described.[2] However, the investigators reported one wave which they attributed to the carbonyl group. As it has been demonstrated that pyridine and pyridine-containing compounds give a reduction wave it was decided to re-investigate the polarographic behaviour of this compound under conditions similar to those used by the previous workers.

The half-wave potentials, the diffusion currents, and the effect of increasing pH on these were essentially the same as reported. However, a second wave was obtained which, contrary to the behaviour of the first, became more negative only in the buffers of pH 6 and 8. Also, as has been observed with other pyridine compounds,[3] the diffusion current of the second wave decreases with increasing pH.

To eliminate the possibility that this second wave might be due to a second reduction process at the carbonyl group, the polarographic reduction of 2-methyl-1,2-di-3′-pyridylpropan-1-ol was investigated in the buffer of pH 2·2. In this experiment only one wave was observed. Its half-wave potential was the same as the second wave obtained with the ketone. The diffusion currents, however, were slightly lower. In all cases, the diffusion currents increased linearly with concentration.

Starka and Buden reported the first wave to represent a 2-electron change which no doubt represents reduction of the carbonyl to an alcohol. Coulometric analysis of the second wave shows a 4-electron change which may indicate the reduction of one double bond in each of the pyridine rings.

Experimental.—McIlvains's buffers or 0·1N-lithium chloride was used as the supporting electrolyte. The dilutions were made from a standard stock solution of 0·001M-2-methyl-1,2-di-3′-pyridylpropan-1-one in the appropriate electrolyte and 0·001M-2-methyl-1,2-di-3′-pyridylpropan-1-ol.

A Leeds and Northrup Type E Electro-Chemograph was used to obtain automatically recorded data. An H-type polarographic cell containing a centrally fused disc was used. One side of this cell contained the standard calomel reference electrode. At a reservoir height of 47·4 cm., $t = 4·0$ sec. and $m = 1·69$ mg. sec.$^{-1}$. The solution was deaerated by passing a stream of nitrogen through it for 5 min. before the recording.

Results are tabulated.

Polarographic data (id, μA) *in McIlvain buffers.*

Ketone concn. (10^{-4}M)	pH 2·2	pH 4·0	pH 6·0	pH 8·0	Alcohol concn. (10^{-4}M)	id (μA)
1	0·28, 2·18	0·42, 1·97	0·55, 1·53	0·69, 0·71	1	2·01
2	0·53, 4·22	0·81, 3·67	1·03, 2·93	1·17, 1·42	2	3·58
3	0·83, 6·20	1·25, 5·61	1·53, 4·23	1·76, 2·28	3	5·31
4	1·25, 8·10	1·63, 7·27	1·84, 5·17	2·14, 3·15	4	7·14
5	1·60, 9·68	2·21, 8·69	2·39, 5·79	2·63, 4·03	5	8·36
$E_{\frac{1}{2}}$ (v)	−0·759, −1·229	−0·850, −1·222	−1·000, −1·303	−1·151, −1·483	$E_{\frac{1}{2}}$ (v)	−1·194

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[3] Kolthoff and Laingane, "Polarography," Interscience, Publ. Inc., New York, 1952, pp. 812—815.

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